

4. ESTIMATING EXPOSURE MEDIA CONCENTRATIONS

4.1. INTRODUCTION

The purpose of this chapter is twofold. First, it describes the algorithms used to determine exposure media concentrations of the dioxin-like compounds. Discussion of the algorithms are structured around three "source categories." These categories roughly translate to beginning points, or origins, of contamination. The source categories are also the basis for the example scenarios described in Chapter 5. Second, it provides information about all the model parameters and justification for the values selected for the demonstration of methodologies in Chapter 5. Parameter discussions appear immediately following descriptions of modeling methodologies.

Section 4.2 provides an introduction to the type of modeling used in this assessment. Section 4.3 describes the algorithms used for the first source category, soil contamination, where the dioxin-like compounds occur in surface soils. The exposures could occur at the site of contamination or the exposures could occur off the site of contamination. Section 4.3 describes the differences in modeling for these two. Section 4.4 describes algorithms to determine exposure media concentrations resulting from stack emissions, the second source category. Chapter 3 laid the groundwork for this section by describing the use of air dispersion/deposition models as applied to a point source to generate two key quantities: air-borne contaminant vapor phase concentrations at a site of exposure, and particulate phase deposition rates. Section 4.4 describes how modeled concentrations and depositions translate to soil, vegetative, and water concentrations. Section 4.5 concludes the chapter with a discussion of algorithms specific to the third source category, point-source effluent discharges into surface water bodies.

Algorithms are presented which estimate exposure media concentrations for: 1) surface soils, 2) surface water impacts: suspended and bottom sediment and dissolved phase concentrations, 3) air including the vapor phase and in particulate form, and 4) biota including beef, milk, fruit and vegetables, and fish.

4.2. BACKGROUND FOR SOLUTION ALGORITHMS

Literally hundreds of fate and transport models have been published which differ widely in their technical sophistication, level of spatial or temporal resolution, need for site specific parameterization, and so on. This can make selection of the most appropriate one for any particular situation difficult. Relatively simple, screening level models are used to model fate, transport, and transfer of dioxin-like compounds from the source to the exposure media in this

assessment. Simple assumptions are often made in order to arrive at the desired result, which is long-term average exposure media concentrations. Perhaps the most critical of the assumptions made is the assumption that the source strength remains constant throughout the period of exposure: the initial soil concentration of dioxin-like compound remains the same for that exposure period, and stack emissions and effluent discharges remain steady throughout this period.

It is important to understand that EPA is not endorsing the algorithms of this assessment as the best ones for use in all dioxin assessments. They are suggested as reasonable starting points for site-specific or general assessments, and as will be discussed shortly, most multi-media exposure modeling has included similar screening level approaches. The assumptions behind models are described carefully throughout this chapter. If these assumptions do not apply to a particular situation, or where assessors require more spatial or temporal resolution, more complex models should be selected. References to other models are made in this and other sections throughout the chapter. Also, Chapter 7 compares the models of this assessment to alternate models for several of the algorithms.

Finally, it cannot be overemphasized that measured concentrations are generally more reliable than modeled ones. Assessors should use measured concentrations if available and if such measurements can be considered spatially and temporally representative for the exposed populations.

The first examples of similar multimedia compartment modeling were probably the "fugacity" models proposed by Mackay (1979) and Mackay and Paterson (1981, 1982). Fugacity in this context is defined as the tendency for a chemical to escape from one environmental media compartment into another. The fugacity of a chemical present in an environmental media compartment is modeled using common fate and transport parameters such as octanol water partition coefficients, Henry's Constants, water solubilities, and so on. The fugacity concept is based on the fact that at equilibrium, equal fugacities are established in all compartments of a system. Examples of fugacity modeling include the transfer of nonionic organic chemicals between the atmosphere and surface water (Mackay, et al., 1986), between the atmosphere and plants (Riederer, 1990), and for food chain modeling (Travis and Hattemer-Frey, 1987). A regional fugacity model being used in regulatory risk assessment forums is the CALTOX (DTSC, 1993) model. Mackay (1991) authored a comprehensive, though somewhat dated, text on multimedia compartment modeling using the fugacity approach.. A key difference between fugacity modeling and the modeling in this assessment is that for fugacity modeling, movement between compartments is considered for both directions - from compartment A to compartment

B and also compartment B to compartment A. The modeling in this assessment is essentially one way - air to leaf, air to soil, vegetation to terrestrial animal, and so forth. This is thought to be reasonable for dioxins under the circumstances for which the models are being promoted - which is the circumstance of the source strength being constant over the period of exposure. Also, because the persistence and adsorptive tendencies of the dioxin-like compounds, movement from one compartment to another tends to be more one-way than it is for less persistent or more volatile organic compounds.

One possible drawback for the fugacity approach applied to the types of source categories discussed in this assessment is that it does not consider spatial variability of concentrations within a compartment. For example, air concentrations vary depending on the distance from a source of air emissions, such as a stack or a site of soil contamination. The fugacity approach would typically treat air as a single compartment with a uniform concentration. This would be a concern for a regional model such as the CALTOX model.

The transfer of contaminants between compartments and multimedia modeling approaches have been extensively studied at the National Center for Intermedia Transport at the University of California, Los Angeles. Their multimedia compartment model, MCM (Cohen and Ryan, 1985), provides several useful algorithms for intermedia transfer factors that would have application for dioxin-like compounds. Later on, this group introduced the spatial multimedia compartment model (Cohen, et al., 1990), which allows for non-uniformity in some compartments. Such a model would be more suitable for the types of source categories of this assessment, since there is non-uniformity within a compartment as noted above in the air compartment example.

An early approach which merged simplistic multimedia modeling with human exposure was termed the exposure commitment method, developed by Bennett (1981). An exposure commitment is defined as a contaminant concentration in human tissue. Exposure commitments are calculated from transfer factors that are estimated as the ratios of the steady-state concentrations of a contaminant in adjoining compartments of an exposure pathway. An example of adjoining compartments is air to plants to livestock to diet. This method has been applied to both PCBs (Bennett, 1983) and 2,3,7,8-TCDD (Jones and Bennett, 1989). These applications have required measured concentrations of the contaminants in different compartments in order to estimate the transfer factors. The retrospective nature of this approach limits its usefulness for general applications.

One of the early multimedia models which also had human exposure as the endpoint, but did not require retrospective data, was the GEOTOX model (McKone and Layton, 1986). This

model had air (vapor and particle phases), water (surface and ground water, including bottom sediments of surface water bodies), soil (soil gas, water, and solid subcompartments), and biomass (eggs, milk, meat, fish, and vegetation including food crops) compartments. The most recent evolution of this model can be found in McKone and Daniels (1991).

Multimedia modeling approaches have been extensively used to evaluate the exposure to dioxins. Paustenbach, et al. (1992) evaluated the exposure and risk to humans from residential and industrial soil contamination by 2,3,7,8-TCDD. Simple models were used to estimate the concentrations of 2,3,7,8-TCDD in air-borne suspended particulates and fish that reside in nearby streams impacted by the contaminated soil. Together with concentrations in contaminated soil, Paustenbach evaluated human exposures via soil ingestion, dermal contact, particulate inhalation, and fish consumption. They also used Monte Carlo techniques on exposure parameters (in contrast to using Monte Carlo on fate and transport parameters) to determine a range of residential and industrial soil concentrations that would result in a specified risk level. The risk level chosen for their demonstration was 10^{-5} , which was determined by multiplication of the Lifetime Average Daily Doses (LADDs in mg/kg-day) and the cancer slope factor for 2,3,7,8-TCDD of $9700 \text{ (mg/kg-day)}^{-1}$ derived by Keenan, et al. (1991). Residential soil concentrations less than 20 ppb did not pose a lifetime cancer risk greater than 10^{-5} . For industrial sites, concentrations in soil that could pose a 10^{-5} risk ranged between 131 and 582 ppb, depending on the amount of time the industrial worker spend outdoors under typical exposure conditions.

Travis and Hattemer-Frey (1991) evaluated human exposure to 2,3,7,8-TCDD from a broader perspective. The principal assumption of the Fugacity Food Chain model used for Travis' human exposure assessment is that atmospheric concentrations of 2,3,7,8-TCDD can be empirically linked to water, soil, and vegetative concentrations, which in turn are linked to agricultural produce, meat, milk, eggs, and fish concentrations. Simple models for atmospheric depositions onto plants, air-to-leaf transfers of vapor phase 2,3,7,8-TCDD onto plants, transfers to cattle beef and milk, and other models, are presented. They also compared their model predictions of exposure media concentrations to literature values, and concluded that their approaches resulted in concentrations comparable to those found in the literature. This effort by Travis and Hattemer-Frey is examined in more detail in Section 5.6 of Chapter 5.

Exposure to 2,3,7,8-TCDD using simplistic multimedia models has also been assessed for specific sources. Goeden and Smith (1989) evaluated the impact to fish and subsequent human exposure by consumption of fish to dioxins and furans emitted by a resource-recovery facility. Surface water sediment concentrations in a lake were estimated as a simple weighted average of concentrations on three kinds of particles entering the lake: soil via erosion whose concentration

was estimated given contaminated particle depositions onto soil (and considering mixing and soil half-lives), deposition of background uncontaminated suspended particulates directly onto the lake, and direct deposition of contaminated particles onto the lake. Fries and Paustenbach (1990) also evaluated the impact of incinerator emissions of 2,3,7,8-TCDD, but they evaluated human exposure via consumption of food crops, meat, and milk. EPA (1990d) used a simple dilution model to evaluate the impact of pulp and paper mill effluent discharges of 2,3,7,8-TCDD and 2,3,7,8-TCDF into surface water bodies.

The air-plant interface has been the subject of numerous fugacity and related modeling efforts for the dioxin-like compounds. This is because it is recognized that this pathway is critical to the terrestrial animal food chain; little soil-to-plant transfer occurs for these highly sorbed class of compounds. Trapp and Matthies (1995) present a comprehensive air/soil-to-plant modeling system, and in their application of this approach to 2,3,7,8-TCDD, they neglect the soil-to-above ground portion of their model. The importance of the vapor phase dioxins has been recognized in numerous modeling efforts, particularly for the lower chlorinated congeners (Lorber, 1995; McLachlan, et al., 1995). McLachlan, et al. (1995) developed a fugacity approach while the empirical air-to-plant transfer factor approach for vapor-phase dioxins in Lorber (1995) is advocated in the methodology.

This is only a cursory summary of the wealth of multimedia modeling approaches that are available, and the application of such modeling approaches for evaluating human exposure to dioxins. While there are many similarities and differences among the approaches, they all share one characteristic in common - they have all been described as "screening level models". Without attempting a definition of the qualifier, "screening level", such a qualifier for these models seems to imply the following types of common features: assumptions of equilibrium and/or steady state conditions between compartments, lack of substantial (if any) spatial or temporal resolution, the use of biotransfer or bioconcentration concepts which simply relate an environmental concentration (air or water concentration, e.g.) to a biomass concentration (plant or fish concentrations), and so on.

A counterpoint to screening level models might be what are termed "mechanistic" models. Such models are more theoretically sophisticated, contain more spatial and temporal resolution, attempt to simulate actual mechanisms of fate and transport rather than depend on empirical relationships developed from data, could involve complex food chain approaches to model biomass concentrations (to counter the simple biotransfer or bioconcentration approaches), and generally are highly parameterized requiring site-specific data that is often not readily available.

Because of the complexity of the multimedia environment, modeling of contaminant fate in such an environment has tended to remain simple. However, there are complex models which can be applied to smaller subsets of the multimedia environment, and which have been applied to assessments of dioxin-like compounds. One example is the ISCST3 model, which was used in this assessment to evaluate the impact of stack emissions of dioxin-like compounds. That model allows for complexities of terrain, varying weather patterns, vapor/particle partitioning, etc., to be considered. It relies on hourly meteorological data to simulate years of atmospheric transport and deposition, and summarizes the results of its simulation as long term average concentrations and depositions. That model is further described in Chapter 3. Another example of more complex modeling was the use of the WASP4 model in a comprehensive evaluation of bioaccumulation of 2,3,7,8-TCDD in Lake Ontario (EPA, 1990b). That application required a substantial amount of site-specific parameterization. Gobas, et al. (1999) describes the application of EcoFate to 2,3,7,8-TCDD and 2,3,7,8-TCDF pulp and paper mill discharges to the Fraser-Thompson River system in British Columbia, Canada from 1988 to 1995. This is a time-dependent, multimedia mass balance simulation of the environmental distribution and food-chain accumulation of organic contaminants in aquatic ecosystems. In this framework, modeled river systems are segmented, and within each segment, numerous compartments are modeled including the bed sediment (an accessible and an inaccessible bed layer), one or several water column compartments, the atmosphere, and one or more aquatic organism trophic levels (algae/zooplankton, benthic filter filters and detritivores, and fish). They were able to demonstrate a successful application of this model to predicted the two dioxin congener concentrations in bottom sediments, rocky mountain white fish, and rainbow trout.

With the exception of the ISCST3 model, the models used for this assessment are better described as screening level rather than mechanistic. Many of the algorithms used are the same or very similar to the ones found in references above. Except for the effluent discharge source category, which uses a non-spatially resolved dilution model for surface water impacts, the algorithms do consider spatial differences between the source and site of impact or site of exposure. For example, the algorithm estimating surface water impacts from a site of soil contamination, while simple in its framework, does incorporate the following: the area of the site that is contaminated, the area of the watershed which drains into the water body, the erosion rates of the site of contamination as well as the rest of the watershed, the proximity of the site to the water body, the concentration of the contaminant at the site of contamination as well as within the watershed other than the contaminated site, the lipid content of the fish, and the organic carbon fractions of the suspended and bottom sediments of the water body. Assignments

for all these parameters impact water and fish concentrations, and it is certainly arguable that they are all site-specific parameters. From this perspective, it could be argued that most of the algorithms of this assessment are generally screening level in their theoretical sophistication, but site specific in their application.

Sections in other chapters of this volume address key issues relating to the use and credibility of the algorithms described in this chapter. Chapter 5, which demonstrates the methodology, makes observations concerning exposure media concentrations. Chapter 6, on user considerations for use of the models and algorithms of this assessment, discusses categorization of model parameters and conducts sensitivity analysis exercises on key fate, transport, and transfer algorithms. Chapter 7 discusses applications of these models in validation exercises, and also compares the models of this assessment to others available for dioxin-like compounds. Chapter 8 on Uncertainty has critical discussions on parameter assignment and algorithm uncertainties.

Figures 4-1 through 4-3 are flow diagrams showing interim compartment concentrations modeled, and principal processes modeled and assumptions made in the intermedia transfer. Sections 4.3. through 4.5 describe the algorithms for the three source categories considered in this assessment, and background and assignment of parameters for the demonstration scenarios of Chapter 5.

4.3. ALGORITHMS FOR THE SOIL CONTAMINATION SOURCE CATEGORY

As earlier noted, exposures to contaminated soils can occur both at the site of the soil contamination or away from the site of soil contamination. Examples of on-site exposure would be worker exposures to Superfund or similar sites, or unique circumstances such as Times Beach where soil at the site of a residence or a playground becomes contaminated. Examples of off-site exposure include exposures at residences, farms, play or school areas, and so on, that are located near, but not at, the site of soil contamination. There are two primary differences with regard to modeling when exposure is on-site versus off-site. One is in the modeling of the dispersion of dioxin residues which have been suspended via volatilization or dust suspension. Models are presented below for on-site dispersion and off-site dispersion. The second difference is that, for on-site exposures, the initial soil concentration is assumed to remain constant throughout the period of exposure. For off-site exposures, the soil concentration at the site of exposure is assumed to build up over time from an initial level of zero before the site became contaminated to a level when exposure begins and then to a second level when exposure ends. The average soil concentration during the period of exposure is estimated as the midpoint between the two

latter concentrations noted. Otherwise, all other algorithms for the soil contamination source category, including the algorithms for surface water impacts and for biota calculations, are the same whether the exposure to the soil contamination is on-site or off-site.

Sections 4.3.1 through 4.3.4 describe the algorithms for estimating concentrations of the dioxin-like compounds in: bottom sediment, suspended solids, and in the dissolved phase in the water column of surface water bodies (4.3.1), exposure site soil concentrations (4.3.2.), in the air in the vapor and particulate phases (4.3.3), and in biota including fish (4.3.4.1), home-grown vegetables and fruit (4.3.4.2), beef and milk (4.3.4.3), and chicken and eggs (4.3.4.4). Section 4.3.5 describes some key characteristics of specific cases of soil contamination.

4.3.1. Surface Water and Sediment Contamination

The principal assumption in the algorithm estimating the impact to surface water and surface water sediments (suspended and bottom sediments) from an area of contaminated soil is that such an impact is correlated to surface soil concentrations at that site as well as surface soil concentrations within a larger area draining into the water body. This drainage area is commonly referred to as a watershed. Further, the impact to the water body is assumed to be uniform. This tends to be more realistic for smaller water bodies as compared to large river systems. Other key assumptions in the surface water impact algorithm are:

- Soil erosion estimates, coupled with sediment delivery ratios, can be used to describe the impact of a contaminated site relative to other soils in the watershed which contribute sediments to the water body;
- The sorption of dioxin-like compounds onto surface soil, suspended solids and bottom sediments is principally a function of the contaminant's organic carbon partition coefficient, K_{oc} , and the organic carbon content of soils and sediments;
- The concentration of contaminants in soil eroding from a site are initially higher than the concentrations at the site itself - it is "enriched" with contaminants. This enrichment occurs because some processes of transport, such as wind erosion or soil erosion, favor lighter soils (silts and clays) which have higher surface area to volume ratios (more binding sites) as well as higher organic matter contents on the average (which also favors more binding of organic chemicals). Other processes such as volatilization or degradation may counteract the enrichment noted at the edge of a site - concentrations on soil entering a water body may be less than those leaving the site;
- The concentration of contaminants in sediment suspended in the water column exceeds the concentration in bottom sediments. Similar reasoning as the above enrichment

argument applies: particulates which remain in suspension tend to be lighter and more enriched with organic matter as compared to particulates which settle to the bottom of water bodies. It should be noted that suspended solids, in this algorithm, are simply a reservoir into which dioxin-like compounds sorb; more complex models consider sorption onto more than one reservoir of suspended materials including suspended particulates and dissolved organic matter;

- Suspended and bottom sediments originate principally as soil erosion; a mass balance is maintained such that a part of the soil reaching the water body through erosion remains as suspended particulates, and a part settles to bottom sediments.

- A steady state is achieved between concentrations in the dissolved phase in the water column, concentrations in the sorbed phase in the water column, and concentrations in bottom sediments;

- Volatilization out of the water body or degradation of residues in the water body are not modeled. Neglecting these dissipation processes has the net effect of overestimating water body impact. On the other hand, bottom sediment resuspension is not modeled. Not modeling resuspension would have a net effect of underestimating water column impacts; and

- Estimating the average impact to the water body, rather than a localized impact which may be the case if the contaminated soil is very near the water body, is suitable for purposes of this assessment procedure.

Concentrations in bottom sediment are desired because fish concentrations are estimated as a function of bottom sediment concentrations (see Section 4.3.4.1). Concentrations in suspended solids are desired because they are used to estimate bottom sediment concentrations, and dissolved phase concentrations are needed for estimating drinking water exposures.

The solution begins with the mass balance statement:

The mass of contaminant entering the water body	=	An amount which remains as dissolved in the water column + An amount which remains sorbed to suspended materials + An amount which remains sorbed to particles settling to the bottom
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This can be described mathematically as:

$$C_{swb} ER_w = C_{wat} V_{wat} + C_{ssed} M_{ssed} + C_{sed} M_{sed} \quad (4-1)$$

where:

C_{swb}	=	concentration on soil entering water body, mg/kg
ER_w	=	total watershed annual soil erosion, kg/yr
C_{wat}	=	dissolved-phase concentration in water column, mg/L
V_{wat}	=	water body annual volume, L/yr
C_{ssed}	=	concentration on suspended sediment, mg/kg
M_{ssed}	=	mass of suspended sediment introduced per year, kg/yr
C_{sed}	=	concentration on sediment settling to bottom, mg/kg
M_{sed}	=	mass of bottom sediment introduced per year, kg/yr

Other equations based on assumptions stated above and needed for this solution are:

1) mass balance of soil is maintained:

$$ER_w = M_{ssed} + M_{sed} \quad (4-2)$$

$$M_{ssed} = f_s ER_w \quad (4-3)$$

$$M_{sed} = (1 - f_s) ER_w \quad (4-4)$$

where:

f_s = fraction of annual erosion remaining as suspended materials, unitless

2) equilibrium between sorbed and dissolved phases is maintained; suspended sediments are enriched in comparison to bottom sediments:

$$C_{wat} = \frac{C_{ssed}}{Kd_{ssed}} \quad (4-5)$$

$$C_{sed} = C_{ssed} \frac{OC_{sed}}{OC_{ssed}} \quad (4-6)$$

where:

Kd_{ssed} = soil-water partition coefficient for contaminant in suspended sediment,
L/kg

OC_{ssed} = fraction organic carbon in suspended sediment, unitless

OC_{sed} = fraction organic carbon in bottom sediment, unitless

Now, Equations (4-2) through (4-6) can be substituted into the right hand side of Equation (4-1) so that this side can be function a one concentration, C_{ssed} , and one erosion amount, ER_w .

Factoring out C_{ssed} then gives:

$$C_{swb} ER_w = C_{ssed} \left\{ \frac{V_{wat}}{Kd_{ssed}} + f_s ER_w + \frac{OC_{sed}}{OC_{ssed}} (1 - f_s) ER_w \right\} \quad (4-7)$$

The bracketed quantity in the right hand side of Equation (4-7) can be termed ϕ , so that C_{ssed} can be solved as $(C_{swb} ER_w)/\phi$. Now, the numerator in this term can be expanded to describe contaminant contributions by a site of contamination and contaminant contributions by the rest of the watershed. Included in this solution is the assumption made above that soils eroding into water bodies are "enriched":

$$C_{swb} ER_w = C_s SL_s A_s E SD_s + C_w SL_w (A_w - A_s) E SD_w \quad (4-8)$$

where:

C_{swb} = concentration on soil entering water body, mg/kg

ER_w = total watershed erosion, kg/yr

C_s = contaminated site soil concentration of dioxin-like compound, mg/kg

E = enrichment ratio, unitless

SL_s = unit soil loss from contaminated site area, kg/ha-yr

A_s = area of contaminated site, ha

SD_s	=	sediment delivery ratio for soil eroding from contaminated site to water body, unitless
C_w	=	average concentration of dioxin-like compound in effective area of watershed not including contaminated site, mg/kg
SL_w	=	average unit soil loss for land area within watershed not including contaminated site, kg/ha-yr
A_w	=	effective drainage area of watershed; the area contributing sediment which mixes with the sediment originating from A_s , ha
SD_w	=	sediment delivery ratio for watershed, unitless

Finally, the right hand side of Equation (4-8) can be termed, ρ , and the concentration in suspended sediment, C_{ssed} , is equal to ρ/ϕ . All the terms in ρ/ϕ are input parameters or can be solved as a function of input parameters. Other water body concentration terms, C_{wat} and C_{sed} , can now be solved using Equations (4-5) and (4-6). Note that this solution is applicable to both stationary water bodies such as ponds or lakes and moving water bodies such as streams or rivers. The differences in the two water systems can be expressed in the parameters, effective watershed area, A_w , water body volume, V_{wat} , and organic carbon contents of suspended solids and bottom sediments, OC_{ssed} and OC_{sed} . Guidance on these terms and assignment of values for the demonstration scenarios in Chapter 5 is now given.

● **C_s and C_w :** These are concentrations of dioxin-like compounds in the contaminated site soil, C_s , and the average within the effective area of the watershed, C_w . The contaminated site concentrations drive the concentrations assumed for most exposures, and is a principal user input. The simplest assumption for C_w is that it is 0.0. However, examination of soil data from around the world shows that, where researchers have measured concentration in what they described as "background" or "rural" settings, soil concentrations of CDD/Fs are in the non-detect to low ng/kg (ppt) range. Chapter 3 of Volume II of these Dioxin Exposure Reassessment Documents describes studies measuring dioxins in rural parts of America and calculates a TEQ_{DFP} -WHO₉₈ of 4 pg/g (ppt). Example Scenarios 1 and 2 in Chapter 5 demonstrate the methodologies in this chapter in what are termed "background" settings. For these example scenarios, the 17 dioxin-like CDD/Fs are initialized to values that have been measured in an actual background setting.

● □ **E:** Enrichment refers to the fact that erosion favors the lighter soil particles, which have higher surface area to volume ratios and are higher in organic matter content. Therefore, concentrations of organic contaminants, which are a function of organic carbon content of sorbing media, would be expected to be higher in eroded soil as compared to in-situ soil. While enrichment is best ascertained with sampling or site-specific expertise, generally it has been assigned values in the range of 1 to 5 for organic matter, phosphorous, and other soil-bound constituents of concern (EPA, 1977). The enrichment ratio would be expected to be higher in sandy soils as compared to silty or loamy soils because the finer silt particles which erode from a soil generally characterized as sandy are more a deviation from the norm compared to silt particles which erode from a soil generally characterized as silty or loamy. The example scenarios in Chapter 5 modeled mid-range agricultural loam soils (as modeled with organic carbon fractions, soil loss parameters as discussed below). The enrichment ratio will therefore be assigned a value of 3.0 in all circumstances.

Two data bases have been found which justify the use of the enrichment ratio in this context. One is the data base from Connecticut which involved the sampling of surface soils and sediments from several rural locations in Connecticut (CDEP, 1992). Enrichment ratios were calculated from individual sites and for three dioxin-like compounds as the ratio of the concentration measured in sediment to the concentration measured in nearby surface soil samples. Enrichment ratios ranged from 0.33 to 12.3 with overall averages for the three dioxin-like compounds of 1.58 (for 2,3,4,7,8-PCDF), 2.59 (2,3,7,8-TCDF), and 3.86 (2,3,7,8-TCDD). Further details on this data are found in Chapter 7. A first set of results from another research study on the Hudson River was described in Smith, et al. (1995). Using modeling, they concluded that the concentration of dioxins in surficial sediment layers of the Hudson River were principally caused by soil erosion: 76% of the total deposition of CDD/Fs to bottom sediments were caused by surface erosion, with other causes including anthropogenic waste (sewer outflows; 20%), and direct atmospheric input (4%). To model the concentrations in the Hudson river surficial sediments, they used an enrichment ratio of 1.6 (defined as here as the ratio of the sediment concentration to the surficial soil concentration), based on an earlier analysis of particle sources of the Hudson river and its tributaries. The data presented in Smith, et al. (1995) on surface soils and sediments also show the disparity between surface soils and sediments - sediment concentrations are higher than surface soil concentration and sometimes substantially higher. However, since the Hudson River watershed is fairly complex and includes important sources other than soil erosion, it would be inappropriate to estimate enrichment ratios from the data as was done for the Connecticut data.

● □ **SL_s and SL_w:** These are the unit soil loss, in kg/ha, from the exposure site and the average from the effective land area draining into the surface water body. In the simplest case, the unit losses can be considered equal. In the most complicated solution, the effective drainage area can be broken up into "source areas", where each source area can be unique in terms of the erosion potential, concentration of contaminant, and so on. The total contribution equals the sum of contributions from each source area, as: $\sum C_j * SL_j * A_j * E_j * SD_j$ for the right hand side of Equation (4-8) for j number of source areas not including the exposure site. For direct input into Equation (4-8), the terms C_j, SL_j, A_j, E_j, and SD_j, should be determined and C_w, SL_w, E_w, and SD_w should be estimated as weighted averages over all source areas, A_j. The effective drainage area, A_w, would be the sum of all source areas, A_j.

For the example scenarios in Chapter 5 demonstrating the “background” settings, SL_s and SL_w are assumed equal. This generally assumes that erosion parameters for the site of exposure mirror the averages for the drainage area. Also, the enrichment ratio, E, is assumed to be constant for all watershed soils. For the demonstration of the soil contamination source category, the site of contamination is assumed to have different erosion characteristics. The following is offered as general guidance and background for estimation of unit soil losses in this assessment.

The unit soil loss is commonly estimated using the Universal Soil Loss Equation. This empirical equation estimates the amount of soil eroding from the edge of a field (Wischmeier and Smith, 1965):

$$SL = R K LS C P \quad (4-9)$$

where:

SL	=	average annual soil loss, Eng. tons/acre-year
R	=	rainfall/runoff erosivity index, t-ft/ac-yr
K	=	soil erodibility factor, t/ac-(unit of RF)
LS	=	topographical factor, unitless
C	=	cover and management practice, unitless
P	=	supporting practices factor, unitless.

Several references are available to evaluate USLE factors for agricultural and non-agricultural settings (EPA, 1977; USDA, 1974; Wischmeier, 1972; Novotny and Chesters, 1981). For this assessment, values for these terms will be based on assumptions about contaminated sites and rural

soils. Justification and assumptions are given below. It should be noted that more sophisticated models are available for estimating erosion rates (i.e., CREAMS as described in Knisel, 1980), and should be considered in actual site-specific assessments.

● **Rainfall/erosivity index, R:** The R term represents the influence of precipitation on erosion, and is derived from data on the frequency and intensity of storms. This value is typically derived on a storm-by-storm basis, but it has been compiled regionally for the development of average annual values (EPA, 1977). Annual values range from less than 50 for the arid western United States to greater than 300 for the Southeast. The value used in this assessment will be 160, which is typical of rainfall patterns seen in much of the midwestern United States.

● **Soil erodibility, K:** The soil erodibility factor reflects the influence of soil properties on erosion, with values ranging from less than 0.05 for non-erodible sandy soils to greater than 0.50 for highly erodible silty soils. The value used in this assessment will be 0.30, which is typical of, for example, sandy or silty loam soils with 2% - 4% organic matter contents.

● **Length-slope factor, LS:** The topographic factor reflects the influence of slope steepness and length of the field in the direction of the erosion. Steeper slopes and longer lengths lead to higher LS values, with a range of 0.1 for slopes less than 1.0% and lengths less than 100 ft to greater than 2.0 for slopes generally greater than 10%. The two key considerations for its assignment, therefore, are the size of the field for which erosion estimates are being made, and the slope of that field. The example scenarios in Chapter 5 had field sizes of 0.4 ha (1 ac) for a rural residence, 4 ha (10 ac) for a small rural farm, and 10 ha (25 ac) for a soil contamination site. Guidance for use of the Universal Soil Loss Equation stops short of defining appropriate sizes of field for which unit estimates are to be derived, except that the USLE was developed for agricultural "fields" where cover, slope, soil type, etc. are assumed to be uniform. For purposes of estimating erosion losses in this assessment, a field of 4 ha for estimating the LS factor will be used. In a rural watershed with agricultural and non-agricultural settings, this would be a reasonable average area of uniformity. If square shaped, a 4 ha area translates to a side length of 200 m. For purposes of assignment of the LS factor, it will be assumed that the contaminated site has a 2% slope. EPA (1977) (and other references as noted above) show nomographs giving the LS factor as a function of slope length and slope. With a 200 meter slope length and a 2%

slope, the LS factor is approximately 0.20. This factor will be used for all soil loss estimates required in this assessment.

● **Support practice factor, P:** The support practice factor reflects the use of surface conditioning, dikes, or other methods to control runoff/erosion. P can be no greater than 1.0. However, values less than 1.0 should only be assigned when specific practices are employed which are designed to reduce erosion. For the example scenarios in Chapter 5, it will be assumed that no such practices are in place at the site of concern or throughout the watershed to control erosion. Therefore, a value of 1.0 will be assumed.

● **Management practice factor, C:** The final term in the USLE is the cover and management practice factor, C, which primarily reflects how vegetative cover and cropping practices, such as planting across slope rather than up and down slope, influences erosion. C values can be no greater than 1.0, with this value appropriate for bare soils. A C value of 1.0 is an appropriate choice for active landfills or sites of high soil contamination (like Superfund sites) mostly devoid of vegetation. For an inactive landfill with grass cover or any area with dense vegetative cover such as grass, a value of 0.1 or less is appropriate. Values greater than 0.1 but less than 0.7 are appropriate for agricultural row crops, which offer more protection than bare soil, but not as much protection as dense vegetation.

Three erosion estimates are required for scenarios demonstrated in Chapter 5. One is for areas of high soil contamination, or the scenario demonstrating the soil contamination source category. It will be assumed that the contaminated site is largely devoid of vegetation in this case, and a value of 1.0 will be assumed. A second erosion estimate is needed to characterize average unit soil loss throughout a watershed draining into a surface water body. The example scenarios are based on a rural setting which has agricultural and non-agricultural (i.e., rural residences) areas. The C value in this circumstance will be assumed to be 0.3. Finally, a soil erosion estimate is needed in the algorithm transporting contaminated soil from an area of high soil contamination to a nearby site of contamination, as part of the algorithms developed for the soil contamination source category. In this case, the land between a site of soil contamination and the nearby site of exposure will be assumed to be covered with dense vegetation, such as grass. In this case, the C value will be 0.1.

As just described, three unit soil loss estimates are required for this estimates and the difference between the three will be expressed in the C term. Multiplication of the five USLE

terms gives unit soil loss estimates of 9.60 (with $C = 1.0$), 0.96 (with $C = 0.1$), and 2.88 (with $C = 0.3$) t/ac-yr. The value of SL_s and SL_w for the demonstration of the background setting scenarios in Chapter 5 is 2.88 t/ac-yr. Since Equation (4-8) and other uses of unit soil loss estimates are needed in kg/ha-yr, these unit losses are easily converted to 21515, 2152, and 6455 kg/ha-yr.

● **A_s and A_w :** These are the area terms, including the area of the contaminated site, and the effective drainage area of the watershed, both in ha. The scenarios demonstrated in Chapter 5 have assumed 0.4 ha (1 acre roughly) for exposure sites described as rural residences, 4 ha (10 acres) for farms, and 10 ha (25 acres) for the site of soil contamination. If the soil contamination site is at the site of exposure, as in the "on-site" source category, then A_s should be assigned an area equaling the site of exposure (and the concentration term, C_s , should equal the average soil concentration over this site of exposure). If the area of contamination is away from the site of exposure, A_s should equal the total area of contamination (and again C_s should equal the average soil concentration over this area).

The total area impacting a river system has been termed a watershed. For purposes of this assessment, an "effective" drainage area will almost always be less than the total area of a watershed. A "watershed" includes all the land area which contributes water to a river system. For large river systems, this area is in the order of thousands of square miles and includes several tributaries and smaller streams feeding into the main branch of the river. Each stream and tributary has its own sub-basin, whose sediment originates from a land area much smaller than thousands of square miles. If the contaminated site lies within that sub-basin, that it would be appropriate to include only the area within that sub-basin as the effective drainage area. This is one circumstance where an "effective drainage area" would be less than a total watershed area. Another consideration for determining the effective drainage area is the positioning of the contaminated site with respect to the point where water is extracted for drinking and fish are caught for consumption. If these points are significantly upstream in the river system in relation to the contaminated site, there is no reason to conclude that sediments or water near where the water is extracted are impacted by the contaminated site. If these withdrawal points are downgradient of the contaminated site, then there is reason to believe that sediments and water are impacted. However, if they are downgradient from the contaminated site but not at the bottom of the watershed, then sediment and water quality further downgradient from the withdrawal points is not of concern and land draining into these downgradient portions would not be part of the "effective drainage area". One further possible consideration is how far upgradient

in the watershed one should go when determining the size of the effective drainage area. While sediments introduced at the furthest points may eventually work their way down to the mouth of the watershed, this may take geologic time and not recent historic time. Therefore, sediment quality near a site of contamination need not consider these far reaches.

For a standing water body such as a lake or a pond substantially fed by ground water recharge, an assumption that probably should be made using the simple framework of this assessment is that all sediments within the lake/pond are completely mixed. Therefore, the effective area should equal all area around the lake/pond contributing sediment, and, as in the above discussion on river systems, a part of the land area contributing sediments to streams or rivers which may feed the standing water body.

From this discussion, it is clear that determination of an effective drainage area depends on site specific considerations, but it will likely be less than the total watershed area. The demonstrations in Chapter 5 assume a reasonably large watershed area draining into a river that can support a fish population suitable for recreational fishing. The effective drainage area of this watershed, A_w , will be assumed to be 100,000 hectares ($1 \times 10^9 \text{ m}^2$, $1 \times 10^3 \text{ km}^2$, 250,000 acres, 385 mi^2). Furthermore, it will be assumed that the water body in question is a river, which mainly impacts the assignment of the total suspended solids parameter, TSS (as discussed below). This assignment is not based on any specific sites that have been studied. As noted, it is justified as being a reasonable size to drain into a river large enough to support recreational fishing.

A useful data source for this term and the suspended sediment term below, for specific sites in the United States, is Appendix F in Mills, et al. (1985). This appendix includes a compilation of data from river and reservoir sediment deposition surveys, including total drainage area, water body volumes, and rates of sediment deposition (mass/area-time). A caution in using this and similar data bases when evaluating specific sites is that, again, these total drainage areas are just that, total areas. Water bodies in this data base are located in the 48 conterminous states. An estimate of suspended sediment concentrations can be made using the water volume and the sediment deposition rates from this data, and an assumption on sediment deposition velocity. The specific weight of sediments in the water body, also supplied in this appendix, can be used to estimate sediment deposition velocity.

● **SD_s and SD_w :** These are the sediment delivery ratios applied to the exposure site and the watershed as a whole. Such a ratio is required because not all the soil which erodes from an area deposits into the receiving water body. The following delivery ratio was proposed for construction sites (EPA, 1977):

$$SD_s = (3.28 DL)^{-0.22} \quad (4-10)$$

where:

- SD_s = sediment delivery ratio for soil eroding from contaminated site to water body, unitless
- DL = distance from contaminated site to receiving water body, m
- 3.28 = converts m to ft (empirical equation was developed for units of ft).

Note that the sediment delivery empirical equation simplifies all land features pertinent to erosion to a function only of length. The equation was developed to estimate sediment loads from construction sites to nearby surface water bodies, and from distances up to 250 m (800 ft, roughly). Without specific information on the sites from which it was developed, it is assumed that the land area between the construction sites and the receiving water body is "average" and this relationship can be used for applications other than construction sites.

As noted in previous bullets, the example scenarios demonstrating the background setting assumed $C_s = C_w$, and $SL_s = SL_w$. The impacted water body was assumed to be 150 meters away from the site of exposure for this demonstration setting. This distance translates to a delivery ratio of 0.26. Site-specific conditions could result in a larger (steeper slope, e.g.) or smaller proportion of the eroded soil being delivered to the water body than would be estimated with this equation.

Figure 4-4 shows a watershed delivery ratio as a function of watershed size. As seen, the ratio decreases as land area increases. The total watershed size, A_w , assumed for the example scenarios in Chapter 5 was 1000 km². From Figure 4-4, this translates to a watershed delivery ratio, SD_w , of 0.06. If the watershed is larger than about 2000 km², which is the extent of coverage of this figure from Vanoni (1975), the following empirical equation was found to satisfactorily extend the relationship seen in Figure 4-4:

$$SD_w = 0.6 (A_w)^{-0.125} \quad (4-11)$$

where:

- SD_w = sediment delivery ratio for a watershed, unitless

A_w = effective drainage area of watershed; the area contributing sediment which mixes with the sediment originating from the contaminated site, m^2

● f_s : As soil erodes into the water body, it will settle onto the bottom to become bottom sediment. Part of the settled material will become resuspended because of turbulent flow. The finest materials in eroded soil may not settle for a long time, and essentially always be in suspension. One way to arrive at the fraction of annually eroding material which remains in suspension ("remains in suspension" for purposes of discussion - in reality, little, if any, will remain in suspension, but will rather deposit and resuspend) involves complex modeling. A wealth of such models exist, such as those described in Wang (1989). The approach used here is more simple than those in Wang (1989).

If an average level of suspended material in the water were specified, in units of mg/L, what would be known with otherwise required parameters is the total amount of erosion reaching the water body (as discussed above) as well as the annual water volume (discussed below). A required parameter for this assessment will therefore be the level of suspended solids in the water body, TSS. With this parameter and the annual water flow volume, V_{wat} , the total suspended load equals, $TSS \text{ (mg/L)} * V_{wat} \text{ (L/yr)}$. The assignment of these two terms are 10 mg/L and $4.8 * 10^{11}$ L/yr, leading to a total suspended load of $4.8 * 10^{12}$ mg/yr, or $4.8 * 10^6$ kg/yr. Total erosion into the water body, in similar units, equals, $A_s * SL_s * SD_s + (A_w - A_s) * SL_w * SD_w$. With parameter assignments as discussed above, the total annual erosion equals $1.29 * 10^7$ kg/yr. Therefore, the fraction of total load that is suspended is 0.36 ($4.8 * 10^6 / 1.3 * 10^7$).

Given this formulation, the f_s term is not a model input value, but is solved on the basis of the other parameters noted.

● **TSS**: This is the total suspended sediment in the water body. This value will be lower for standing water bodies such as ponds or lakes as compared to streams or rivers. The more turbulent flow in rivers will suspend sediments to a greater degree than a relatively calm lake. A complex modeling exercise evaluating the impact of 2,3,7,8-TCDD to Lake Ontario assumed a suspended sediment concentration of 1.2 mg/L (EPA, 1990b). For use in pond or lake settings, an assumption of a suspended sediment concentration of 1-2 mg/L is reasonable. All example scenarios in Chapter 5 assume that the 100,000 ha watershed drains into a river suitable for supporting fish for consumption and water for drinking purposes. General guidance offered for the potential for pollution problems in rivers and streams as a function of average suspended sediment concentration are: 10 mg/L or less - no problem, 100 mg/L or less - potential problem,

and greater than 100 mg/L - probable problem. A cutoff concentration for protection of aquatic life is 80 mg/L (Mills, et al., 1985). The value assumed for TSS for all example scenarios in Chapter 5 is 10 mg/L, indicating no turbidity problems and a river supportive of fish for consumption.

- V_{wat} : The stream in the example scenarios will be assumed to derive its annual flow only from the effective drainage area, A_w . Given the area of drainage, one way to estimate annual flow volume is to multiply total drainage area (in length squared units) times a unit surface water contribution (in length per time). The *Water Atlas of the United States* (Geraghty et al., 1973) provides maps with isolines of annual average surface-water runoff, which they define as all flow contributions to surface water bodies, including direct runoff, shallow interflow, and ground-water recharge. The range of values shown include 5-15 in/yr throughout the Midwest cornbelt, 15-30 in/yr in the South and Northeast, 1-5 in/yr in the desert Southwest, and a wide range of 10-40 in/yr in the far West. For this assessment, an assumed 19 in/yr is used to estimate the annual flow volume. Over a 100,000 hectare drainage area, total flow volume equals 4.8×10^{11} L/yr ($19 \text{ in/yr} * 0.0254 \text{ m/in} * 100,000 \text{ ha} * 10,000 \text{ m}^2/\text{ha} * 1000 \text{ L/m}^3$).

- Kd_{ssed} : This adsorption partition coefficient describes the partitioning between suspended sediment and the water column. For numerous applications for organic contaminants, particularly for estimating the partitioning between soil and soil water, this partition coefficient has been estimated as a function of the organic carbon partition coefficient and the fraction organic carbon in the partitioning media:

$$Kd_{\text{ssed}} = Koc \cdot OC_{\text{ssed}} \quad (4-12)$$

where:

- Kd_{ssed} = soil-water partition coefficient for contaminant in suspended sediment, L/kg
- Koc = organic carbon partition coefficient for contaminants, L/kg or cm^3/gm
- OC_{ssed} = fraction organic carbon content of suspended sediment, unitless.

The organic carbon partition coefficient, Koc , can be a measured value or it can be estimated. Chapter 2 of Volume II of this dioxin exposure reassessment reviewed the available

literature on Koc for 2,3,7,8-TCDD. Based on available studies measuring the Koc, a log Koc value of 6.6 was recommended for this congener. Recommendations could not be made for the other dioxin-like congeners because of few measured data points, and when available, the data sometimes showed considerable differences.

In the absence of measured values, the Koc can be estimated from a chemical's octanol water partition coefficient, Kow. Empirical equations relating Kow to Koc are listed in Lyman, et al. (1982). Of six different equations listed in that reference, the following derived by Karickhoff, et al. (1979) is used to estimate the Koc for the example compounds in Chapter 5:

$$\log Koc = \log (Kow) - 0.21 \quad (4-13)$$

where:

Koc = organic carbon partition coefficient, L/kg
 Kow = octanol water partition coefficient, unitless

This equation was empirically developed from a limited number of hydrophobic contaminants (n=10, R² = 1.00). It implies that Koc is very similar to Kow for strongly sorbed compounds such as the dioxin-like compounds. Using the log Kow of 6.8 recommended in Chapter 2, Volume II of this assessment for 2,3,7,8-TCDD, the estimate of log Koc is 6.59. This is essentially the same as the recommendation for log Koc of 6.6 for 2,3,7,8-TCDD based on measurement studies. This relationship will be used to estimate the Koc for all other dioxin-like compounds.

● □ **OC_{sed}, OC_{ssed}:** The organic carbon content of solids and sediments of water bodies are generally higher than organic carbon contents of the surrounding lands. Furthermore, organic carbon contents of suspended organic materials and solids are typically greater than those of bottom sediments. A significant sink for strongly hydrophobic contaminants such as the dioxin-like compounds is thought to be suspended, or non-settling, organic material. In modeling 2,3,7,8-TCDD in Lake Ontario (EPA, 1990b) using the WASP4 model, a compartment separate from suspended solids termed "non-settling organic matter" served as a permanent sink. For purposes of this assessment, a single reservoir of suspended materials onto which incoming dioxin-like compounds sorb is principally characterized by OC_{ssed}, and the values selected for OC_{sed} and OC_{ssed} should reflect the relative partitioning behavior of suspended and bottom materials. As noted above, these water body carbon contents are also related to the organic

carbon contents of surrounding soils. The model parameter, OC_{sl} , is the soil organic carbon fraction and is required for modeling of soil contamination by dioxin-like compounds. Foth (1978) lists the organic nitrogen content of several soil types ranging from sand and sandy loam to clay. The range from that list is 0.0002 - 0.0024 on a fractional basis. Assuming a carbon to nitrogen ratio of 10 (Brady, 1984; who notes that C:N ratios vary from 8 to 15, with the typical range of 10 to 12), organic carbon ranges from 0.002 to 0.024. A soil organic carbon fraction, OC_{sl} , is assumed to be 0.01 for all example settings in Chapter 9, which is in the middle of this range. The organic carbon content of bottom sediments, OC_{sed} , will be higher at 0.03. Bottom sediments originate as erosion from surrounding land, but also include decay of organic materials within water bodies. The organic carbon content of suspended materials can approach 0.20, but OC_{ssed} will be assumed to be 0.05 for the example settings in Chapter 5.

4.3.2. Exposure Site Soil Concentrations

If the soil contamination occurs at the site of exposure, than the exposure site soil concentration is simply the soil concentration as initialized by the model user. As described in the Section 4.3.1 above, a key assumption for the simplistic models used in this assessment is that the source strength does not vary over the course of the exposure. Therefore, the soil concentration as initialized remains unchanged during the exposure period. An example of a situation where the contaminated soil is at the site of exposure is a residential property impacted similar to the properties at Times Beach, Missouri, where residential soils were impacted by the spraying of waste oils for dust suppression. Another example would be the analysis of worker exposures on a Superfund site contaminated by dioxin-like compounds.

A more typical application of the methodologies for soil contamination, however, would be the circumstance where sites of exposure are near, but not at, the site of soil contamination. For example, residences or farms near a Superfund site would be the scenario of concern for the contaminated soil source category. This section describes methodologies for estimating the soil concentration at an exposure site near a contaminated soil site.

The key assumptions for the solution strategy estimating exposure site soil concentrations resulting from an off-site soil contamination source are: 1) the exposure site soil becomes contaminated due to erosion of contaminated soil from the source to the exposure site, 2) the amount of soil at the exposure site does not increase, which means that soil delivered to the site via erosion is matched by an equal amount which leaves the site, and 3) not only does soil erode off the contaminated site en route to the exposure site, but soil between the contaminated site and the exposure site also erodes to the exposure site.

The second and third assumption translate to:

$$D_1 + D_2 = SR \quad (4-14)$$

where:

- D_1 = mass of soil delivered from off-site contaminated source, kg
- D_2 = mass of soil delivered from land area between contaminated source and exposure site, kg
- SR = mass of soil removed from exposure site, kg.

The mass balance equation for exposure site soil concentrations can now be qualitatively stated as (with " ΔC " used as shorthand for change in exposure site soil concentration over time):

- ΔC = (the incremental addition to C resulting from the change in erosion of contaminated soil) -
- (the incremental subtraction of C resulting from removal of now contaminated soil from the exposure site) -
- (the incremental subtraction of C resulting from dissipation of residues at the exposure site)

This can be expressed mathematically as:

$$\frac{dC_e}{dt} = \frac{D_1 C_s}{M} - \frac{SR C_e}{M} - k_s C_e \quad (4-15)$$

where:

- C_e = the exposure site soil concentration, mg/kg
- D_1 = mass of soil delivered from off-site contaminated source, kg/yr
- C_s = contaminated site soil concentration of dioxin-like compound, mg/kg
- M = mass of soil at exposure site into which contaminant mixes, kg
- SR = mass of soil removed from exposure site, kg/yr
- k_s = first order soil dissipation rate constant, 1/yr.

Assuming that the contaminant concentration at the exposure site, C_e , is initially 0, Equation (4-15) can be solved to yield:

$$C_e = \frac{D_1 C_s}{SR + k_s M} \left[1 - e^{-\left(\frac{SR}{M} + k_s\right) t} \right] \quad (4-16)$$

which computes C_e as a function of time, t (in years since k is in years). This can be solved for various increments of time starting from a time when the exposure or contaminated site initially became contaminated, or it can be simplistically assumed that the contamination has existed at the contaminated site for a reasonably large amount of time such that the exponential term approaches zero. The rate at which the exponential term approaches zero is a function of the value of k , the first-order dissipation constant. The smaller the value of k (i.e., the longer the half-life of dioxins transported to a nearby site), the longer it will take for the system to reach steady state. The algorithms of this assessment, such as the surface water algorithms described above and the calculation of the biota calculations as described below, have simplistically assumed that steady state has occurred by the time any exposure has occurred. This simplicity will be continued here. Generally, assuming steady state will lead to conservative results - i.e., overall impacts over time will be less if the systems modeled have not reached steady state (or close enough to it) by the time exposure begins. At steady state, the exponential term drops out, and C is estimated as:

$$C_e = \frac{D_1 C_s}{SR + k_s M} \quad (4-17)$$

One final note on this solution is that, unlike the solution for estimating water body impacts, there is not an assumption that the eroded soil is enriched in comparison to the soil at the site of contamination; an enrichment ratio was used in the surface water algorithm, but not for this algorithm. The foundation for enrichment of sediments was the arrival of finer textured soils with higher concentrations of constituents of concerns (organic contaminants, inorganic nutrients) at water bodies. This theory is well founded and there is data on the enrichment of dioxin-like compounds in sediments as compared to surface soils. On the other hand, there is no

similar evidence or foundation for assuming enrichment for dioxin-like compounds in soil when the transport is to a nearby site instead of a more distant water body.

Equation (4-17) was used to estimate exposure site concentrations resulting from the erosion of contaminated soil in the demonstration of the soil contamination source category in Chapter 5. Guidance for estimation of these terms including justification for their values as selected in the example settings are:

- k_s : For soil residues at the site of soil contamination, the assumption is made that residues do not degrade or dissipate to the point of reducing the concentration of the "initial" soil levels. This was partly based on information indicating generally low rates of biological or chemical degradation for the dioxin-like compounds of this assessment, coupled with the assumption that the soil contamination was sufficiently deep implying a reservoir of contaminant that would remain available during a period of exposure. These assumptions are less likely to be valid for residues which have migrated over the surface to deposit on the exposure site. The deposition is likely to result in only a thin layer of contaminated soil. Though very small, surface-related dissipation mechanisms such as photolysis, volatilization, or degradation, might reduce surface soil contaminant concentrations. For these reasons, a "dissipation" rate constant is assumed to apply to delivered contaminant, where the precise mechanisms of dissipation are not specified, but could include transport (volatilization, erosion) and degradation (photolysis) mechanisms.

Fries and Paustenbach (1990) suggested the use of a half-life of at least 10 years, and used a 15 year half-life in their example scenarios on the impact of air-borne deposition of 2,3,7,8-TCDD originating from stack emissions. In a later publication, Paustenbach, et al. (1992) reviewed the literature on the environmental half-life in soil. For surface soils, they cited the evidence from Eglin Air Force Base (Young, 1983) suggesting a half-life of 10 to 12 years for 2,3,7,8-TCDD, and the work of Cerlesi, et al. (1989), who estimated a soil half-life of 9.1 years for 2,3,7,8-TCDD in Seveso soil. Paustenbach, et al. (1992) also discussed the fact that the loss of TCDD from soil is predominantly through volatilization and photodegradation of residues at the soil surface, and that loss mechanisms are minimal below the soil surface. They suggested that ultraviolet radiation penetrates only about the surface 0.1 cm, which implies that photodegradation could be limited below that depth. They concluded that their review supported the concept that TCDD probably has a half-life of 9-15 years in surface soil and 25-100 years in subsurface soils. McLachlan, et al. (1996) reported on an analysis of soil taken from experimental plots which had been amended with sewage sludge in 1968 and sampled in 1972,

76, 81, 85, and 90. These archived samples were analyzed for all 17 dioxin-like CDD/Fs, and based on an analysis of results, McLachlan and coworkers concluded that half-lives were on the order of 20 years, with dioxin removal from the plots being mainly physical removal processes (overland runoff, wind erosion). Furthermore, their results suggested that all congeners had been removed at roughly the same rate, which is why they concluded that removal processes were mainly physical and very little in-situ degradation appeared to be occurring.

This assessment assumes that residues transported from a site of soil contamination to a site of exposure mix in a soil layer extending 2 cm. This will be discussed below. Therefore, the reservoir of dioxin-like compounds includes a surficial component and what could be considered a subsurface component. This suggests that the average half-life of residues within this depth might be greater than the 9-15 year estimate for surface soils by Paustenbach, et al. (1992), but less than the 25-100 year estimate made by these researchers. This assessment will assume a half-life of 25 years for the 2-cm reservoir of transported dioxins, which translates to a k_s of 0.0277 yr^{-1} . Ideally, half-lives should be assigned to individual dioxin-like congeners as many of the other contaminant-specific parameters such as K_{ow} or bioconcentration parameters. However, the data for 2,3,7,8-TCDD was not definitive, and based on McLachlan's findings with sewage sludge amended soils, it appears reasonable to assign the same half-life to all congeners. The uniform rate of degradation, k_s , for all CDD/Fs, and PCBs, will be 0.0277 yr^{-1} .

● **M:** The delivered contaminant mixes to a shallow depth at the exposure site. The mixing depth depends on activities which disturb the surface, such as construction, plowing, vehicle traffic, movement of cattle or other animals, burrowing action of animals, other biological activity, normal leaching, and raindrop splash. Mixing depths for fallout plutonium have been found to be 20 cm on cultivated land and 5 cm on uncultivated forest and rangeland (Foster and Hakonson, 1987). Fries and Paustenbach (1990) suggested a depth of 15 cm for agricultural tillage, but assumed values of 1 and 2 cm for various sensitivity tests. However, they did not need to make a distinction between tilled and untilled situation because vegetation (pasture grass and forage for estimating beef and milk fat concentration; above ground fruits and vegetables for human consumption) was assumed to be impacted only by particulate deposition and not root uptake. In another assessment on indirect impacts from incinerator emissions, EPA (1990a) estimated vegetation concentrations as a function of particulate depositions, root uptake, and air-to-leaf transfer from the vapor phase. Different mixing depths for untilled and tilled concentration estimation was required. For root uptake estimation for vegetable and other crops, the estimated soil concentrations assuming a tillage mixing depth of 20 cm. For soil

concentrations in untilled situations, they assumed a mixing depth of 1 cm. This mixing depth of 1 cm was retained in a later addendum to this methodology (EPA, 1993a). An earlier version of these dioxin exposure methodologies assumed a 1 cm depth for untilled soils and a 20 cm depth for tilled soils (EPA, 1994).

The methodology of this assessment uses 2 cm for the untilled and 20 cm for the tilled conditions for the off-site soil source category. A principal justification for the increase from the 1 cm depth of the earlier dioxin exposure assessment methodologies (EPA, 1994) to the current 2 cm depth for surface soils comes from Brzuzy and Hites (1995). Their data on soil concentrations of dioxin congener groups as a function of depth show definite migration of residues below the surface. Soil core results were described and concentration versus depth was displayed for 6 cores. The cores were undisturbed, and were taken in background settings with high vegetative cover so that the introduction of dioxins was speculated to be due only to atmospheric depositions - not pesticides or in an oily matrix. Briefly, the results did show a relationship between leaching and percent organic carbon - more residues near the surface soil at higher organic carbon content. For the 6 cores displayed: 1) a peak at the 1-2 cm depth was found in only one core, 2) there was essentially uniform concentrations for 3 cores to 5 cm with dropoffs thereafter, and 3) in two cores which had low organic carbon, there was a steadily rising concentration to peaks at 45 and 55 cm. The authors speculated that downward movement was due to movement of soil particles. They also did suggest that based on their sediment core information that deposition to these soils had been occurring for 60 years. This is not likely to be analogous to the situation of soil eroding from a site of soil contamination both because of the time involved and the mechanism of transport. Still, it would appear from this data that a 1 cm depth may not be justifiable. Based on this evidence, an untilled depth assumed for the soil contamination source will be 2.0 cm.

A tilled depth will be assumed to be 20 cm, as in earlier assessments (EPA, 1990a; EPA, 1993a; EPA, 1994). This assumption is made because tilling gardens is assumed to distribute surface residues to the 20-cm depth. Soil concentrations for dermal contact, soil ingestion, and pasture grass and soil intake for cattle grazing will assume a depth of 2 cm. These activities are assumed to occur on soil which has not been tilled. As will be described in Section 4.5, tilled and untilled depths of mixing are also required for the stack emission source category. For that source category, the untilled and tilled mixing depths are also assumed to be 2 and 20 cm, respectively.

Given the area of the exposure site, the mass of soil into which the eroded contaminant is mixed can be calculated as:

$$M_u = A_{es} B_{soil} d \quad (4-18)$$

where:

M_u	=	mass of soil for contaminant mixing per unit depth, kg/m
A_{es}	=	area of exposure site, m ²
B_{soil}	=	soil bulk density, kg/m ³
d	=	depth of mixing, m

● **D₁ and D₂:** The first step in deriving both these amounts of soil is to use the Universal Soil Loss Equation (USLE). This approach was described above. Justification was given for an assumption of unit soil loss from the contaminated site of 9.6 t/ac-yr in Section 4.3.1. D₁ equals this unit loss times the area of contamination times a sediment delivery ratio. The example scenario in Chapter 5 assumed that the exposure site was 150 meters from the contaminated site, and using Equation (4-10), the sediment delivery ratio is 0.26. The unit loss assumed for the area between the contaminated site and the exposure site is 0.96 t/ac-yr. Since this area is adjacent to the exposure site, there is no sediment delivery, and D₂ equals this unit loss times the area between the contaminated and exposure sites.

D₁ and D₂ can now be expressed as:

$$D_1 = 0.224 SL_1 SD_1 A_s \quad (4-19a)$$

$$D_2 = 0.224 SL_2 SD_2 A_{BLE} \quad (4-19b)$$

where:

$D_{1,2}$	=	mass of soil delivered from off-site contaminated source, D ₁ , and from the land area between contaminated source and exposure site, D ₂ , kg/yr,
$SL_{1,2}$	=	average annual unit soil loss, Eng. tons/acre-year, equal to 9.6 t/ac-yr for SL ₁ and 0.96 t/ac-yr for SL ₂
$SD_{1,2}$	=	sediment delivery ratios, unitless, 0.26 for SD ₁ (with distance = 150 meters) and 1.00 for SD ₂

- A_S/A_{BLE} = land area of contaminated site, A_S , and of area between contaminated site and exposure site, A_{BLE} , m^2
 0.224 = converts t/ac-yr to kg/m^2 -yr.

An adjustment is made to the sediment delivery ratio, SD_1 , considering the size discrepancies between the contaminated site and the exposure site. For example, if the contaminated site is larger than the exposure site, then the amount of eroded soil delivered 150 meters downgradient would not all mix with soil at the exposure site. On the other hand, if the contaminated site were smaller than the exposure site, than the full amount of eroded soil delivered 150 meters downgradient would be contained within the exposure site. A simple correction factor, equaling the ratio of a side length of the exposure site (assumed square-shaped) and a side length of the contaminated site size (also assumed square shaped), is used to adjust the sediment delivery ratio:

$$SD_{1a} = SD_1 CF_{SD} \quad (4-20)$$

where:

- SD_{1a} = adjusted sediment delivery ratio corresponding to SD_1 , unitless
 SD_1 = sediment delivery ratio reducing the amount eroding from the contaminated site to be delivered to the exposure site, unitless
 CF_{SD} = sediment delivery correction factor, unitless
 = $A_{ES}^{0.5}/A_S^{0.5}$ if $A_{ES} < A_S$
 = 1 if $A_{ES} > A_S$
 A_{ES} = area of exposure site, m^2
 A_S = area of contaminated site, m^2

Similar considerations are pertinent to the land area between the contaminated and exposure site. Remember that the algorithm assumed that some "clean" (D_2) and some "contaminated" soil (D_1) erodes onto the exposure site, and that a similar amount of soil entering the exposure site (R , which equals $D_1 + D_2$) leaves the exposure site so as to maintain a mass balance. The amount of clean soil eroding from upgradient sources mixing with exposure site soil can be larger than the amount of contaminated soil if the exposure site is larger than the

contaminated site. If the exposure site is smaller than the contaminated, and similar to the solution for SD_{1a} above, then only the small corridor defined by the size of the exposure site contributes clean soil. Either way (i.e., the exposure site is larger or smaller than the contaminated site), the size of the land area contributing clean soil is defined by the size of the exposure site. A_{BLE} can be estimated as the product of the distance between the exposure and contaminated site, and the side length of the exposure site:

$$A_{BLE} = DLCE \ SLE \quad (4-21)$$

where:

A_{BLE}	=	land area between contaminated and exposure site, m^2
DLCE	=	distance from contaminated site to exposure site, m
SLE	=	side length of exposure site, m
	=	$(A_{es})^{0.5}$
A_{es}	=	area of exposure site, m^2

4.3.3. Vapor- and Particle-Phase Air Concentrations

The algorithms for estimating vapor- and particle-phase concentrations of contaminants were presented and derived in Hwang, et al. (1986), EPA (1985b), Hwang (1987), and Turner (1970). The algorithms, in general, entail estimation of the flux of vapor phase and particle bound dioxin-like compounds, and then the estimation of the dispersion of fluxes to arrive at appropriate air concentrations. The flux calculations for emissions of vapor phase and particle bound dioxin-like compounds is the same if the soil contamination occurs at the site of exposure or away from the site of exposure. However, the dispersion algorithms differ, depending on whether the site of exposure is at the site of contamination or away from the site. Discussions below begin with the procedure for calculating the soil fluxes, the volatile flux and the wind erosion flux, of dioxin-like compounds, and then to the two different dispersion algorithms.

The procedures for estimating volatile flux were developed for soil surface and subsurface contamination with polychlorinated biphenyls, PCBs. The models are based on the assumptions that: 1) PCBs move through the soil primarily by vapor phase diffusion, i.e., leaching is not considered, 2) PCB vapor in the soil matrix reaches a local equilibrium with pore air, 3) degradation processes for PCBs were not considered, and 4) the PCB contamination

occurs at the surface and extends down infinitely. These assumptions are similar to the general types of assumptions that have been made for all the algorithms estimating exposure media concentrations in this assessment. The procedures in that PCB assessment were also used for this assessment. Details of the derivation are presented in Hwang, et al. (1986).

The average flux rate over an exposure duration of ED can be estimated as:

$$FLUX_v = \frac{(2) (E_{slp}) (D_{ea}) (C_s) (H) (41) (10^{-6})}{Kd_s [(\pi) (I) (ED)]^{0.5}} \quad (4-22)$$

where:

FLUX _v	=	average volatilization flux rate of contaminant from soil, g/cm ² -s
E _{slp}	=	soil pore porosity, unitless
D _{ea}	=	effective diffusivity of contaminant in air, cm ² /s
C _s	=	contaminant concentration in soil, ppm or mg/kg
H	=	Henry's Constant of contaminant, atm m ³ /mol
Kd _s	=	soil/water partition coefficient, cm ³ /g
ED	=	exposure duration, s
I	=	interim undefined term for calculation, cm ² /s
	=	[D _{ea} E _{slp}] / [E _{slp} + P _{soil} (1-E _{slp}) [Kd _s /(41 H)]]
P _{soil}	=	particle bulk density of soil, g/cm ³

The effective diffusivity, D_{ea}, is solved as a function of contaminant diffusivity in air, and soil pore porosity:

$$D_{ea} = D_c E_{slp}^{0.33} \quad (4-23)$$

where:

D _{ea}	=	effective diffusivity of contaminant in air, cm ² /s
D _c	=	molecular diffusivity of contaminant in air, cm ² /s
E _{slp}	=	soil pore porosity, unitless.

The soil adsorption partition coefficient, Kd_s , is given as:

$$Kd_s = Koc OC_{sl} \quad (4-24)$$

where:

Koc = contaminant organic partition coefficient, L/kg
 OC_{sl} = fraction organic carbon in soil, unitless.

It is noted in Hwang, et al. (1986) that this procedure would tend to overestimate emissions and resulting exposures in situations involving small spills which would not involve deep contamination. It is also noted that the average flux rate is inversely proportional to the square root of the duration of exposure - the longer the duration of exposure, the lower will be the average flux rate. Whereas this solution assumes an unlimited reservoir of contaminant, it is an unsteady state solution (unlike most other solution strategies) and is essentially an average flux rate over an amount of time defined by the exposure duration. Inherent in the solution was the consideration that residues dissipate by volatilization at the surface layers, resulting in contaminants diffusing upwards from deeper soil layers over time. With this longer path of diffusion, volatilized amounts decrease, and hence the average flux over time also decreases.

The method for determining the flux of soil particles due to wind erosion for on-site conditions was developed in EPA (1985b) based on Gillette's (1981) field measurements of highly erodible soils. A key assumption for this solution is that the soil surface is assumed to be exposed to the wind, uncrusted, and to consist of finely divided particles. This creates a condition defined by EPA (1985b) as an "unlimited reservoir" and results in maximum dust emissions due to wind only. This solution will, in essentially all cases, overestimate the amount of dioxin-like compounds being emitted by wind erosion. This is because the soil conditions to which it applies, uncrusted and consisting of finely divided particles, are conditions that, at the very least, are disrupted by rainfall or anthropogenic activities (plowing, walking, etc.). The degree of overestimation is less in the situation of most concern - mostly unattended sites of high soil contamination. An alternate, less conservative solution, is one described as a "limited" reservoir solution. This model is presented in EPA (1989). A major problem with this model for application in the current framework is that it requires site-specific daily rainfalls and windspeeds, and it should be run for a period of time, at least a year, in order to estimate average

daily flux. To be consistent with all other methodologies of the soil contamination source category, and to be conservative regarding dust emissions, the “unlimited” reservoir solution is used here. This wind erosion flux for the unlimited reservoir approach is given as (EPA, 1985b):

$$E_e = 0.036 (1 - V) (U_m/U_t)^3 F(x) \quad (4-25)$$

where:

- E_e = total dust flux of <10 μm particle due to wind erosion, $\text{g}/\text{m}^2\text{-hr}$
- V = fraction of vegetation cover, unitless
- U_m = mean annual wind speed, m/s
- U_t = threshold wind speed, m/s
- $F(x)$ = a function specific to this model.

EPA (1985b) provides details allowing for the application of this equation under a variety of circumstances. Specific parameter assignments for the application of this equation to the example scenarios in Chapter 5 are given below.

The unit dust flux is easily converted to a contaminant flux by multiplying by soil concentration:

$$FLUX_{WE} = (2.8 \times 10^{-17}) C_s E_e \quad (4-26)$$

where:

- $FLUX_{WE}$ = contaminant wind erosion flux from soil, $\text{g}/\text{cm}^2\text{-s}$
- E_e = total dust flux of <10 μm particle due to wind erosion, $\text{g}/\text{m}^2\text{-hr}$
- C_s = contaminant concentration in soil, ppb or ng/g
- 2.8×10^{-17} = converts $\text{ng}/\text{m}^2\text{-hr}$ to $\text{g}/\text{cm}^2\text{-sec}$.

Like for vapor-phase dioxin-like compounds, the flux is converted to a concentration by the use of a dispersion term. Hwang (1987) describes an algorithm for the dispersion of contaminants emitted from an area source. Vapor- and particle-phase concentrations along the

center ($y=0.0$) of this area source are used to estimate concentrations when the site of exposure is at the site of contamination:

$$C_{vp} = \frac{(2/\pi)^{0.5} FLUX a 10^{10} erf(e)}{u_m S_z} (e^{-0.5 (z/S_z)^2}) \quad (4-27)$$

where:

- C_{vp} = vapor- or particle-phase concentration of contaminant in air, $\mu\text{g}/\text{m}^3$
- FLUX = average volatilization or wind erosion flux rate (FLUX_v or FLUX_{WE}) of contaminant from soil, $\text{g}/\text{cm}^2\text{-s}$
- a = side length of contaminated site parallel to the wind direction, m
- U_m = mean annual wind speed, m/s
- S_z = vertical dispersion coefficient in air, m
- z = height of the exposed individual, m
- erf = error function
- e = error function term, unitless
- = $b/(2*(2*S_y)^{.5})$
- b = side length perpendicular to the wind direction, m
- S_y = horizontal dispersion coefficient in air, m
- 10^{10} = converts $\text{g}/\text{cm}^2\text{-m}$ to $\mu\text{g}/\text{m}^3$.

The dispersion terms, S_z and S_y can be estimated using site-specific wind rose data. In the absence of data, these terms can be estimated assuming the most common stability class, D, as:

$$S_y = 0.1414 X^{0.894} \quad (4-28a)$$

$$S_z = 0.222 X^{0.725} \quad (4-28b)$$

where:

- $S_{y,z}$ = horizontal and vertical dispersion coefficient, m

X = distance upwind of the contaminated site, m

Estimating the dispersion and resulting exposure site concentrations of air-borne contaminants, originating at a site of contamination which is near but not at the site of exposure, requires a different solution than this solution for the concentrations along the center line of an area source. A simplified solution, given as a virtual point source model, can be found in Turner (1970). This model approximates the dispersion that occurs from an area source by using an imaginary point source. This point is located upwind of the actual source at a distance calculated to create a lateral dispersion at the site equal to its width:

$$C_{vp} = \frac{2.03 \text{ FLUX } A_{sc} \text{ FREQ } 10^{10}}{VD S_z U_m} \quad (4-29)$$

where:

- C_{vp} = vapor or particle phase concentration of contaminant in air, $\mu\text{g}/\text{m}^3$
- FLUX = average volatilization or wind erosion flux rate (FLUX_v or FLUX_{WE}) of contaminant from soil, $\text{g}/\text{cm}^2\text{-s}$
- A_s = area of contaminated site, m^2
- FREQ = frequency wind blows from source to receptor, unitless
- VD = virtual distance, source center to receptor, m
- S_z = vertical dispersion coefficient, m
- U_m = average wind speed, m/s
- 10^{10} = converts g/cm^2 to $\mu\text{g}/\text{m}^2$.

The term, FREQ, is not in the original Turner (1970) solution. It has been added to this equation to appropriately account for changing wind directions, and hence, obtain a more accurate annual average air concentration. The vertical dispersion, S_z , is estimated as an empirical function of the distance from the source center to receptor:

$$S_z = 0.222 x^{0.725} - 1.7, \quad x < 1000 \text{ m} \quad (4-30a)$$

$$S_z = 1.260 x^{0.516} - 13.0, \quad x > 1000 \text{ m} \quad (4-30b)$$

where:

S_z = vertical dispersion coefficient, m
 X = actual distance from source center to receptor, m.

The virtual distance, VD, is an empirical function of the width of the contaminated area and the actual distance from source center to receptor:

$$VD = 2.514 b + x \quad (4-31)$$

where:

VD = virtual distance, source center to receptor, m
 b = width of contaminated area perpendicular to wind direction - defined previously as side length for assumed square-shaped contaminated area, m
 X = actual distance from source center to receptor, m.

Background on K_{oc} and OC_{sl} were given in Section 4.3.1. above. Guidance for other terms in the four algorithms - volatile flux, wind erosion, on-site dispersion, off-site dispersion, now follow.

● **E_{slp} :** Porosity is defined as the pore space in soils occupied by air and water, and for sandy surface soils show a range of 0.35-0.50. Medium to fine-textured soils (loams, clays, etc.) show a higher range of 0.40-0.60 (Brady, 1984). Soil porosities in the example settings were 0.50.

● **H:** Henry's Constants were discussed in Volume 3, Chapter 2. The values of H used for the three example compounds were: for 2,3,7,8-TCDD - 3.29×10^{-5} atm-m³/mole; for 2,3,4,7,8-PCDF - 4.98×10^{-6} atm-m³/mole; and for 2,3,3',4,4',5,5'-HPCB - 6.65×10^{-5} atm-m³/mole.

● **P_{soil}**: Particle bulk density is defined as the mass of a volume of soil solids. This contrasts the more common parameter, bulk density, which is the mass of a unit of dry soil, which includes both pores and solids. Particle bulk density, P_{soil}, has a narrow range of 2.60 to 2.75, and for general calculation purposes, Brady (1984) recommends a value of 2.65 for average mineral surface soils, the value used for the example settings.

● **ED**: The exposure duration is simply the amount of time individuals are exposed. Two exposure durations were used in the demonstration scenarios, 9 years for "central" and 30 years for "high end" exposures. Used in this algorithm, and as discussed earlier, longer exposure durations translate to lower average volatilization fluxes. This presumes a soil concentration assumed to be uniform over depth starting at time zero, and to become depleted over time. The selected exposure durations of 9 (2.83*10⁸ sec) and 30 years (9.46*10⁸ sec) was used.

● **D_c**: Molecular diffusivities in air of the example compounds could not be found in the literature. However, diffusivities of one compound can be estimated from another with the following (Thibodeaux, 1979):

$$\frac{D_a}{D_b} = \left(\frac{MW_b}{MW_a}\right)^{0.5} \quad (4-32)$$

where:

D_{a,b} = Molecular diffusivities of compounds a and b, cm²/s

MW_{a,b} = Molecular weights of compounds a and b, g/mole

Thibodeaux (1979) lists the molecular diffusivity of diphenyl at 25 °C at 0.068. Given the molecular weight of diphenyl of 154 g/mole, the diffusivities of the example compounds are: 2,3,7,8-TCDD (MW = 322) = 0.047; 2,3,4,7,8-TCDF (MW = 340) = 0.046; and 2,3,3',4,4',5,5'-HPCB (MW = 396) = 0.043.

● **U_m :** Mean annual windspeeds vary from between 2.8 and 6.3 m/s (EPA, 1985b). An assumption of 4.0 m/s in the absence of site-specific average wind speeds was made for the example scenarios of this assessment.

● **a, b, z, and x:** Simple assumptions can be made to assign values to the length terms above: a, b, z, and x. Assuming a square-shaped contaminated site, a equals b which equals the square root of the area of the site. A common assumption for z, the height of the exposed individual, is 2 m. The x term can be assumed equal to a side length (a or b), or can equal the side length plus the distance to the exposed individual if the contamination is not on-site and dispersion is modeled as "near field." For the residence and farm setting examples in Chapter 5, where the contamination was on-site, the x term was equal to a side length.

● **FREQ:** Where the wind blows from all directions equally, then it will blow from one compass sector about 15% of the time. On these bases, a FREQ of 0.15 was used in the example scenario demonstrating the soil contamination source category in Chapter 5. In most places, however, wind direction is much less variable, and the appropriate value is best determined with site specific information.

● **V:** Chapter 5 demonstrates "background" conditions for a "residence" and a "farm". In those settings, grass or crops are likely to substantially cover the soil, and the fraction of vegetative cover can range from 0.5 (minimal coverage) to 0.9 (more lush coverage). For the residence example setting in Chapter 5, V was set at 0.9 which assumes a continual grass cover over the contaminated soil. The V for the farm settings was instead 0.5. The area of contamination for the example farm settings was larger than the residence setting, 10 acres to 1 acre. The land where crops were grown was also contaminated; the 0.5 value for V assumes that the cropland is totally or partially bare at some times - perhaps during spring land preparation and fall harvest. For the demonstration of the soil contamination source category, the site of contamination is assumed to be bare, as in an active landfill or an industrial site. With this assumption, V is set equal to 0.0.

● **U_t :** As noted above, the average windspeed, U_m , is assumed to be 4.0 m/s. The threshold wind velocity, U_t , is the wind velocity at a height of 7 m above the ground needed to initiate soil erosion. It depends on nature of surface crust, moisture content, size distribution of

particles, and presence of non-erodible elements. It can be estimated on the basis of the following procedure (EPA, 1985b):

Step 1. Determine the Threshold Friction Velocity

This is the wind speed measured at the surface needed to initiate soil erosion. EPA (1985b) shows how it can be determined as a function of soil aggregate size distribution. However, for the "unlimited reservoir" approach for which Equation (4-25) was developed, soil particles are assumed to be fine at 1.5 mm or less as an average. This translates to a threshold friction velocity of 75 cm/s and less. A value of 50 cm/s might be reasonably assumed to be representative of these types of surfaces, and was assumed for this assessment.

Step 2. Estimate the "Roughness Height"

EPA (1985b) graphically shows the roughness height for a range of possible conditions. Included in this range are a roughness height of 0.1 cm for natural snow, 1.0 cm for a plowed field, 2.0-4.0 cm for grassland, 4.0 cm for a wheat field or for suburban residential dwellings, and up to 1000 cm for high rise buildings. The assumption made for the residence and farm example settings was 4.0 cm, following the information given for a wheat field or a suburban residence. The value assumed for the site of contamination in the demonstration of the soil contamination source category was 1.0 cm, which assumes that the plowed field value is the most analogous to the assumed bare soil site of contamination.

Step 3. Estimate Ratio of Threshold Wind Speed at 7 m to Friction Velocity

A chart provided by EPA (1985b) shows this ratio as a function of roughness height. For a roughness height of 4.0 cm, this ratio is seen to be 13. For a roughness height of 1.0 cm, this ratio is 16.5.

Step 4. Estimate Threshold Wind Speed

This is simply the product of the ratio given in step 3 above and the friction velocity. Using values given above, $50 \text{ cm/sec} * 13 = 6.5 \text{ m/sec}$ for the residential and farm settings, and 8.25 m/sec for the site of soil contamination.

● **F(x):** The model-specific function, $F(x)$, is determined by first calculating the dimensionless ratio x , where $x = 0.886 U_T/U_m$, and finding $F(x)$ from a chart of $F(x)$ versus x , as

provided in EPA (1985b). For $U_t = 6.5$ and $U_m = 4.0$, $x = 1.44$ and $F(x) = 1.05$. For $U_t = 8.25$ and $U_m = 4.0$, $x = 1.83$ and $F(x) = 0.5$.

4.3.4. Biota Concentrations

This section summarizes the algorithms to estimate contaminant concentrations in fish, vegetation (including vegetables for human consumption and pasture grass or fodder grown on contaminated soil for beef cattle consumption), beef, and milk. As will be shown, all algorithms are simple empirical equations which relate an environmental media concentration to a biota concentration, using a "biotransfer" or "bioaccumulation" factor.

4.3.4.1. Fish Concentrations

The procedure and supportive data for the algorithm to estimate fish tissue concentrations can be found in Cook, et al. (1991), in an assessment of risk of 2,3,7,8-TCDD to aquatic life and associated wildlife (EPA, 1993b) which EPA is conducting as part of its reassessment of dioxin-like compounds, and most recently in a technical support document for the Great Lakes Water Quality Initiative (EPA, 1995). Of those references, only EPA (1995) contains information on the suite of dioxin-like (and other) compounds.

Dioxin-like compounds share a high degree of hydrophobicity that increases as the degree of chlorination increases. Cook, et al. (1991) note that this corresponds in general to an increase in lipophilicity and an increase in ability to bind to organic carbon in sediments and to dissolved organic matter in water. However, these tendencies are not paralleled by an increase in bioaccumulation. Only the 2,3,7,8-chlorine-substituted congeners are substantially bioaccumulated by fish, although large quantities of other CDD/F congeners are found in sediments. This pattern of bioaccumulation results because of higher rates of metabolism of CDD/Fs in fish as compared to the 2,3,7,8-chlorine-substituted congeners (EPA, 1992a; Cook, et al., 1991, with references to Muir et al., 1986; Gobas, 1990). While the highly chlorinated 2,3,7,8-substituted congeners are very slowly accumulated, they have very slow elimination rates.

2,3,7,8-TCDD and other planar polyhalogenated aromatic hydrocarbons often have not been detected in water from aquatic ecosystems even when biota are highly contaminated. Because surface layers of bottom sediments are a good indicator of the relative amount of chemical in the system over the time scale involved for bioaccumulation of super-hydrophobic chemicals, a term known as the Biota to Sediment Accumulation Factor, or BSAF, has been offered as a measure of site-specific bioaccumulation potential. This term was proposed to

replace equivalent terms which were known as the Bioavailability Index, or BI (Kuehl, et al., 1987; Cook, et al., 1991; EPA, 1990b), the Accumulation Factor, AF (Lake, et al., 1990) and the Biota to Sediment Factor, or BSF (Parkerton, et al., 1993; Parkerton, 1991). BSAF is defined as:

$$BSAF = \frac{C_{lipid}}{C_{oc}} \quad (4-33)$$

where:

BSAF	=	biota to sediment accumulation factor, unitless
C_{lipid}	=	concentration of contaminant in lipid of fish, mg/kg,
C_{oc}	=	concentration of contaminant in bottom sediment organic carbon, mg/kg

The surface water algorithms estimate concentration of contaminant in bottom sediments (see Section 4.3.1 above). This concentration, C_{sed} , can be converted to an organic carbon basis as a function of OC_{sed} :

$$C_{oc} = \frac{C_{sed}}{OC_{sed}} \quad (4-34)$$

where:

C_{oc}	=	concentration of contaminant in bottom sediment organic carbon, mg/kg;
C_{sed}	=	concentration of contaminant in bottom sediment, mg/kg;
OC_{sed}	=	fraction organic carbon in bottom sediment, unitless

The organic carbon content of bottom sediments was assumed to 0.03; see Section 4.3.1. for the derivation of C_{sed} .

Since the accumulation of contaminant is assumed to occur only in fish lipid, a correction term to estimate the whole fish tissue concentrations is needed since fish consumption in g/day refers to whole fish consumption. The correction term is simply f_{lipid} , and so whole fish concentrations are simply $C_{lipid} * f_{lipid}$.

The BSAF was developed as a measure of bioaccumulation potential rather than as a predictor, as it is being used here. It is uncertain as to whether measured BSAFs are generally applicable to other water bodies. Efforts are underway to evaluate the general applicability of BSAFs (P. Cook, Duluth Environmental Research Laboratory, US EPA, 6201 Congdon Boulevard, Duluth, MN 55804, personal communication). Using the BSAF approach as a predictive tool greatly underplays the complexity of the processes transferring contaminants from aquatic ecosystems to aquatic organisms. EPA (1993b and 1995) provides a comprehensive discussion on aquatic impacts and processes for dioxin-like and related compounds. Following are some of the key issues to consider:

1) **Resident vs. Migratory Species:** Parkerton (1991) applied a bioenergetics-based bioaccumulation model in an attempt to duplicate BSAFs for 2,3,7,8-TCDD found for carp and blue crabs in the Passaic River, New Jersey. He showed nearly a ten-fold difference in 2,3,7,8-TCDD BSAF calculated from data for resident species as compared to migratory species in the Passaic River. This would be expected for fish which also reside part of the time in relatively clean water bodies; migration would enable depuration of residues from fish. The possibility that migration patterns might explain some of the results for fish concentrations of 2,3,7,8-TCDD in the Lake Ontario bioaccumulation study was also raised (EPA, 1990b). That assessment also discussed a related issue of concern - to consider lakewide average sediment concentrations or concentrations near where sampled fish were captured in calculating the BSAF. Even within a large lake, more sedentary populations of fish may be impacted by localized contamination.

2) **Past history of contamination:** If contamination of surface water bodies with hydrophobic compounds like the dioxin-like compounds has occurred principally in the past, then it can be expected that most of the contamination occurs in or near the bottom sediment layer and not within the water column. Furthermore, if inputs to water bodies are declining or low in comparison to past loadings, then sediments would be undergoing depuration - residue levels would be declining, and the system may not be equilibrium. EPA (1990b) noted that very low BAF*s (defined as a fish to sediment ratio not including the sediment organic carbon and fish lipid considerations of BSAFs) and BSAFs for 2,3,7,8-TCDD in Lake Ontario contrasts higher BAF*s for other hydrophobic compounds such as DDE or PCBs. An explanation offered is that loadings to the Lake may be declining, such that there is a substantial disequilibrium between sediments, water, fish, and their prey. One parameter required in the bioenergetics model Parkerton (1991) used (referred to in the above bullet) was a ratio of contaminant

concentration in bottom sediment to that in suspended sediment, rs/rw . In modeling exercises on the Passaic River, he found closer agreement between measured and predicted BSAFs with this ratio equal to 10 in contrast to 1, the only two values tested; a ratio of ten means that the concentration of contaminant in bottom sediment is ten times higher than it is in the suspended sediment. BSAFs predicted by the model were developed as the ratios in modeled fish lipid concentrations divided by modeled bottom sediment organic carbon normalized concentrations. Measured BSAFs used actual Passaic River fish lipid and bottom sediment concentrations of 2,3,7,8-TCDD. BSAFs predicted with this ratio equal to 1 were roughly 4 times as high as measured BSAFs, and BSAFs found with rs/rw equal to 10 were twice as high as measured. A related result of his modeling exercise was that, at best fit between modeled and measured BSAFs where the rs/rw was 10, dietary exposures explained over 50% of the BSAFs for carp and 85% in blue crabs, in contrast to water column exposures. He speculates that prey organisms consist of benthic animals which ingest contaminated bottom sediment. If the food chain begins near bottom sediments, and if food chain exposures are a principal explanation for fish tissue dioxin concentrations, then it follows that a model would perform better when bottom sediment concentrations drive fish tissue concentrations rather than water column concentrations, or equivalently, when $rs/rw = 10$. Finally, he notes that 2,3,7,8-TCDD contamination in Passaic river largely occurred as a result of historical loadings. The picture that emerges from Parkerton's modeling is as follows: sediments are serving as an internal source of contaminants due to past historical loadings, and the water column is in disequilibrium with bottom sediments and driven only by depuration of bottom sediment concentrations. The bioaccumulation of these compounds in carp and blue crabs appears to be mediated by trophic transfer via the benthic foodweb. In both the Lake Ontario and Passaic River studies, concentrations of 2,3,7,8-TCDD were higher in deeper bottom sediments as compared to surficial bottom sediments - this implies historical loadings and possibly depuration of surficial residues.

This issue is non-trivial for the methodology of this assessment, since an assumption for deriving suspended and bottom sediment concentrations is that the contamination is ongoing, and that the hypothetical water body may be closer to a state of equilibrium as compared to situations where contamination was principally in the past. The BSAF assumed for 2,3,7,8-TCDD in the demonstration scenarios of 0.09 is more in line with data from EPA (1990b) on Lake Ontario and from Parkerton (1991) from data in Passaic River, then with other data (presented later) where historical loadings are not as clear a principal source of bottom sediment contamination. The issue of ongoing versus historical contamination should be considered when assigning site-specific BSAFs.

3) **Variations among fish species, particularly column feeder vs. bottom feeder:** Feeding habits, age, migratory patterns, and lipid contents (including lipid content of edible vs. inedible fish tissues) are just a few of the interacting factors which determine a site-specific BSAF as a function of fish species. Bottom-feeders such as carp or catfish can have BSAF values that could be an order of magnitude higher as compared to column feeders. A calculated 2,3,7,8-TCDD BSAF for carp in Connecticut of 0.86 compares to the 2,3,7,8-TCDD BSAF of 0.03-0.07 calculated for trout by EPA (see Table 4-1). The demonstration of this approach in Chapter 5 assigns a single BSAF to each of the three example contaminants, and the assignment is expected to be more like BSAFs for column feeders. Although not unlike other simplifications of this assessment, such approaches are recognized as oversimplifications.

4) **Study designs to obtain BSAFs:** Although there is some evidence that BSAFs specific to a contaminant may be applicable to other aquatic settings, data to evaluate such a hypothesis is still sparse. Even data sets that do exist need to be carefully evaluated before deriving BSAFs. Such an evaluation should consider sediment as well as fish species data. Critical factors for sediment sampling include location, number, depth of sampling, variability, availability of organic carbon fraction information, and so on. Similar issues are pertinent for fish sampling and analysis.

Following now are guidance for the terms required for estimating fish tissue concentrations.

● **BSAF:** Table 4-1 summarizes literature from which biota sediment accumulation factors for dioxin and furan congeners could be developed. Only six sets of data were found in the literature. The data reported in EPA (1995) for Great Lakes Trout, from the Wisconsin River (Kuehl, et al. 1987), and that from 1 lake in Sweden (Kjeller, et al. 1990) both show decreasing BSAF with increasing chlorination. The BSAF of 2.94 for 2,3,7,8-TCDD determined from a lake in Sweden should be questioned since it is more than an order of magnitude different than any of the other data. Causes for this discrepancy could be manifold. Some observations from Kjeller, et al. (1990) might shed some light on this result. Although sediment data was from three water bodies, 8 of the 9 Pike samples (pike samples were composites of 2-5 fish from one location in the water body) were from one of the water bodies. This is why only data from the one water body was summarized in Table 4-1. This water body, Lake Vanern, was clearly the most contaminated of the three water bodies studied. A paper mill was located at the northern part of this lake and the authors concluded that discharges from this mill impacted the lake. The

average of 2,3,7,8-TCDD and 2,3,7,8-TCDF organic carbon normalized concentrations for five sediment samples from this lake was 297 pg/g; the analogous average concentration for 10 samples taken from another lake, Lake Vattern (6 samples), and a river, Dala (4 samples), was 65 pg/g. A similar disparity between Lake Vanern and the other water bodies is found with the penta-CDD/F concentrations: 205 pg/g vs. 108 pg/g, with similar comparisons for the hexa-, hepta, and octa-CDD/CDF. The sediment and corresponding pike sample nearest this mill had the highest concentrations reported - pike samples were given as 3000 and 833 pg/g lipid normalized 2,3,7,8-TCDF and 2,3,7,8-TCDF (a composite from 5 pike taken at this sampling station), respectively, and sediment was 1800 and 244 pg/g organic carbon normalized for 2,3,7,8-TCDF and 2,3,7,8-TCDD. Note the BSAF for 2,3,7,8-TCDD implied from this data point is 3.41. Another consideration for high BSAFs might be the source of contamination. Speculation from the Lake Ontario and Passaic River field data was that contamination principally occurred in the past, whereas in the Swedish data, contamination appears to have been ongoing at the time of sampling. This might be one indication that BSAFs for aquatic systems where contamination is ongoing might be greater than from systems where the contamination is primarily historical.

The Swedish data also illustrates some of the complexities of interpreting literature data. First, the sediment data was expressed concentrations normalized to "sediment contents of organic material" (sic). This was interpreted as organic matter normalized, not organic carbon normalized. Parkerton (1991) assumed that organic carbon was 45% of organic matter to derive BSAFs when organic carbon data was unavailable; following this lead, organic matter normalized concentrations in Kjeller, et al. (1990) were divided by 0.45 to arrive at organic carbon normalized concentrations. Also, there was not an exact match in "sites" between sediment samples and fish samples; these sites were physical locations within the large lake where samples were taken. There were five sites where sediment samples were taken, and five sites where composited pike samples were taken in Lake Vanern. However, one of the sediment and one of the pike samples were from unique sites; only four sites had both sediment and pike samples. The results in Table 4-1 were derived using average sediment and pike concentrations from only these four sites. Another way to have derived BSAFs would be to average all lake sediment and pike concentrations; since there may be some relationship between sediment and pike concentrations based on lake location, it was decided to include only the four sites with both fish and sediment samples. Finally, there were two sets of results listed for 1,2,3,4,6,7,8-HpCDF as though there were two unique sets of analyses for the same congener; this is why there are two entries for this congener in Table 4-1.

A complete discussion of the data generated by the Connecticut Department of Environmental Protection (CDEP, 1992) is included in Chapter 7. Generally, water bodies tested were mostly in rural/suburban settings rather than urban settings. Concentrations of 2,3,7,8-TCDD in surface soils and bottom sediments were in the low ppt level, indicating background impacts. BSAFs generated with that data ranged from 0.24 to 0.85 for TEQs, 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 2,3,4,7,8-PCDF.

EPA (1995) published BSAFs for lake trout for the 17 dioxin-like congeners based on a reanalysis of the Lake Ontario sediment and lake trout samples originally taken in 1987-88 and reported on first in EPA (1990). It is not clear how many of the samples were reanalyzed and why the 2378-TCDD lake trout BSAF was different in the 1995 report, 0.059, as compared to the 1990 report, 0.07. EPA (1995) also discussed the concept of the “bioequivalency factor”, or BEF, which is defined as the ratio between the BSAF of each non 2378-TCDD dioxin-like congener to the BSAF of 2378-TCDD. These BEFs are listed in Table 4-1. They can be used to assign congener-specific BSAFs if all that is known for a specific site is the 2378-TCDD BSAF.

Excluding the Swedish data, there are 43 reported BSAFs for dioxin-like congeners in Table 4-1. These range from 0.00065 to 0.93, with lower BSAFs associated with higher chlorinated congeners. A BSAF of 0.09 will be assumed for 2,3,7,8-TCDD in the demonstration scenarios in Chapter 5. The BSAFs for the other dioxin-like congeners will be assigned based on the BEF for that congener. For example, the BSAF of 2,3,4,7,8-PCDF will be equal to 0.14, which is estimated as the BEF for 2,3,4,7,8-PCDF, 1.6, times the BSAF for 2,3,7,8-TCDD.

EPA (1990b) estimated BSAFs for PCBs and other selected chemicals (DDE, HCB, etc.) for Lake Ontario from several data sets. Later, EPA (1995) reported on BSAFs for subsets of the dioxin-like congeners from three data sets: Oliver and Niimi (1988), a reanalysis of their own sediment and lake trout samples from the 1988 Lake Ontario study, and the EPA Green Bay/Fox River Mass Balance Study. Parkerton, et al. (1993) summarizes BSAFs for PCBs and other compounds from other water bodies using other data sets. A selected summary of BSAFs for PCBs taken from the two EPA references and the Parkerton, et al. (1993) reference is given in Table 4-2.

Two trends are apparent. First, the BSAFs for PCBs appear to exceed those of the dioxin and furan congeners by an order of magnitude and more. Second, and from limited data, it would appear that BSAFs increase from dichloro- through hexa- or perhaps hepta-chloro PCBs, and then decrease thereafter. An assignment of a BSAF for 2,3,3',4,4',5,5'-HPCB, which is abbreviated as PCB 189 in the IUPAC system, is not apparent from the data summary below. Two data points from EPA place the value for that congener at 0.71 and 3.45. The data point

from Siskiwit for the single heptachloro-PCB, which was 2,2',3,4',5,5',6-HPCB, was estimated by Parkerton, et al. (1993) as 12.5. The BSAF for the heptachloro-PCB congener group for flounder from New Bedford Harbor estimated by Parkerton, et al. (1993) was 0.84, with BSAFs for lobster and crab as 1.29 and 2.74, respectively. A value of 2.10 is assigned to 2,3,3',4,4',5,5'-HPCB for the example scenarios in Chapter 5, which is the midpoint of the two EPA data points specific to this congener

It should be noted that these assignments are based on data on vertebrate rather than invertebrate aquatic species. It is generally recognized that invertebrates do not possess the enzymatic capability to metabolize hydrophobic compounds as effectively as higher chordates. As a result, invertebrate species such as mussels, clams, oysters, shrimp, crabs and lobsters may have BSAF values much higher than those observed for fish. Parkerton (1991) and Parkerton, et al. (1993) reviewed the literature to estimate BSAFs of 1 to 5 for species including grass shrimp, sandworms, deposit feeding clams, and blue mussel for CDD/Fs and PCBs.

Finally, it should be noted that all bioconcentration or biotransfer parameters, such as the BSAF, are qualified as second order defaults for purposes of general use. Section 6.2. of Chapter 6 discusses the use of parameter values selected for the demonstration scenarios, including a categorization of parameters. Second order defaults are defined there as parameters which are theoretical and not site-specific, but whose values are uncertain in the published literature. The parameter values in this category should be considered carefully by users of the methodology.

- f_{lipid} : Lipid contents of edible fish species have been compiled in EPA (1995), and for the sake of brevity, this compilation will not be repeated here. Generally, lipid contents can range from 0.05 to greater than 0.20 (5% - 20%). BSAFs are typically developed on the basis of whole fish lipid content, so estimates of whole fish concentrations should be made with a whole fish lipid content. Parkerton, et al. (1993) cautions, however, that lipid contents of edible portions of fish may be lower than lipid contents of some of the fish portions that were sampled and used to develop BSAFs. Non-edible high lipid content portions include, for example, liver and hepatopancreas. Parkerton, et al. (1993) develops the parameter, β , which is defined as the ratio of the lipid content of the edible portion and the sampled tissue. To demonstrate the impact of this ratio, Parkerton used data from Niimi and Oliver (1989) which included PCB and other halocarbon compound concentration in whole fish and fillets of fish taken from the Great Lakes. The β (defined here as the ratio of lipid in fillet to lipid of whole fish) for these fish, which included brown trout, lake trout, rainbow trout, and coho salmon, ranged from 0.22 to 0.51. The ratio of fillet to contaminant concentrations ranged from 0.20 to 0.54.

In the context of the current model, concentrations in fish for estimating exposure are estimated as the product of: organic carbon normalized bottom sediment concentrations * BSAF * f_{lipid} . BSAFs (in theory) are independent of fish tissue being sampled - they are ratios of the organic carbon normalized concentration and fish lipid concentration. Users should be aware, however, that the f_{lipid} value assigned should correspond to the fish concentration of interest - that could be whole fish if the model is used in validation exercises or edible fish if the model is used for exposure assessment. Cook, et al. (1990) and EPA (1993b) assumed a lipid content of 0.07 for fish in discussions of BSAF and related methodologies for estimating bioaccumulation of 2,3,7,8-TCDD in aquatic ecosystems. This assessment will also assume a f_{lipid} of 0.07, and since its use in this context is in exposure assessment, this value could be thought of as a edible portion lipid fraction.

4.3.4.2. *Vegetation Concentrations*

Vegetation concentrations are required for the estimation of exposure to homegrown fruits and vegetables, and also for the beef and dairy food chain algorithms. Three principal assumptions are made to estimate vegetative concentrations:

- □ Outer surfaces of bulky below ground vegetation are impacted by soils which contain dioxin-like compounds. Inner portions are less impacted than outer portions, although data has shown some within plant translocation into below ground vegetables.
- □ Translocation of dioxin-like compounds from roots to above ground portions of plants are negligible compared to other mechanisms which impact above ground portions of plants. As such, translocation into above ground portions will be assumed to be zero.
- □ Unlike below ground vegetables, data has shown very little impact to inner portions of above ground bulky vegetation. Therefore, it will be assumed that outer and not inner portions of above ground bulky vegetation are impacted.

Concentration of contaminants in below ground vegetation is only required for vegetables (carrots, potatoes, e.g.) grown underground. The basis for the below ground algorithm is the experiments of Briggs, et al. (1982) on uptake of contaminants into barley roots from growth solution, and their elaboration of a Root Concentration Factor. The below ground concentration is given by:

$$C_{bgv} = \frac{C_s RCF VG_{bg}}{Kd_s} \quad (4-35)$$

where:

- C_{bgv} = fresh weight concentration of below ground vegetables, pg/g
- C_s = contaminant concentration in soil, ppt or pg/g
- Kd_s = soil-water partition coefficient, L/kg
= $Koc * OC_{sl}$
- Koc = contaminant organic partition coefficient, L/kg
- OC_{sl} = fraction organic carbon in soil, unitless.
- RCF = root concentration factor equaling the ratio of the contaminant concentration in roots (fresh weight basis) and the concentration in soil water, unitless
- VG_{bg} = empirical correction factor for below ground vegetation which accounts for the differences in the barley roots for which the RCF was derived and bulky below ground vegetables, unitless

Two processes, air-borne vapor phase absorption and air-borne particle deposition, are assumed to contribute to above ground vegetation concentrations:

$$C_{abv} = C_{vpa} + C_{ppa} \quad (4-36)$$

where:

- C_{abv} = concentration in above-ground vegetation, expressed on a dry weight basis, pg/g or ppt
- C_{vpa} = contribution of concentration due to vapor-phase absorption or airborne contaminants, pg/g or ppt
- C_{ppa} = contribution of concentration due to wet plus dry deposition of contaminated particulates onto plant matter, pg/g or ppt

The basis for a vapor-phase transfer factor for various airborne contaminants, including 1,2,3,4-TCDD, from the atmosphere to vegetation was developed by Bacci, et al. (1990, 1992), with amendments suggested by McCrady and Maggard (1993), and McCrady (1994). The final values selected for the 17 dioxin-like CDD/Fs were developed by calibration (Lorber, 1995), and then field validated (Lorber and Pinsky, 1999), as described below. Bacci and coworkers conducted laboratory growth chamber experiments on the vapor-phase transfer of 14 organic

compounds from air to azalea leaves, and developed a generalized model to predict the vapor-phase bioconcentration factor based on a contaminant Henry's Constant, H, and octanol water partition coefficient, K_{ow}. A similar experiment by McCrady and Maggard (1993) conducted for 2,3,7,8-TCDD vapor transfer to grass leaves suggested that the Bacci empirical algorithm to would greatly overestimate the transfer factor for 2,3,7,8-TCDD. The development of the biotransfer factor for vapor-phase dioxins, termed B_{vpa} in this assessment, was based on field data. Further details on these experiments are in the section below on this critical parameter. The algorithm estimating plant concentrations as a function of vapor-phase air concentrations is:

$$C_{vpa} = \frac{B_{vpa} C_v VG_{ag}}{d_a} \quad (4-37)$$

where:

- C_{vpa} = plant concentration due to vapor-phase absorption or airborne contaminants, pg/g or ppt, dry weight basis
- B_{vpa} = mass-based air-to-leaf biotransfer factor, unitless [(pg contaminant/g plant dry)/(pg contaminant/g air)]
- C_v = vapor-phase concentration of contaminant in air, pg/m³
- VG_{ag} = empirical correction factor which reduces vegetative concentrations considering that B_{vpa} was developed for transfer of air-borne contaminants into leaves rather than into bulky above ground vegetation
- d_a = density of air, g/m³, 1190

Several exposure efforts for 2,3,7,8-TCDD (Fries and Paustenbach, 1990; Stevens and Gerbec, 1988; Connett and Webster, 1987; Travis and Hattemer-Frey, 1991), have modeled the accumulation of residues in vegetative matter (grass, feed, vegetables) resulting from deposition of contaminated particulates. Key components of their approach, as well as the one for this assessment, include:

- □ Vegetative concentrations result from particulate deposition onto plant surfaces.
- □ Vegetative dry matter yield is the reservoir for depositing contaminants; this reservoir varies according to crop.

- Not all particulate deposition reaches the plant, some goes directly to the ground surface; the "interception fraction", less than 1.0, reduces the total deposition rate. This fraction can be related to the percent ground that is covered by the vegetation.

- Weathering processes, such as wind or rainfall, remove residues that have deposited onto plant surfaces via particle deposition, and this process is reasonably modeled as a first-order exponential loss with an associated weathering dissipation rate. All the above references have justified a dissipation rate derived from a half-life of 14 days (based principally on field measurements described in Baes, et al. (1984)); this is the value used for all dioxin-like compounds in this assessment as well. As well, a portion of particles depositing as wet deposition are not retained on the vegetation after the rainfall. A retention factor reduces total wet deposition considering this.

- Vegetative concentrations may not reach steady state because of harvesting or grazing, but a steady state algorithm is used.

The steady state solution for plant concentrations attributed to wet plus dry particle deposition is:

$$C_{ppa} = \frac{F_p}{1000 k_w Y_j} \quad (4-38)$$

where:

- C_{ppa} = plant concentration due to settling of contaminated particulates onto plant matter, pg/g or ppt, dry weight basis
- F_p = unit contaminant wet plus dry deposition rate onto plant surfaces, pg/m²-yr
- k_w = first-order weathering dissipation constant, 1/yr
- Y_j = dry matter yield of crop j, kg/m²
- 1/1000 = converts pg/kg to pg/g

The unit contaminant wet plus dry deposition rate, F , is given as:

$$F_p = C_p (V_d I_j + RN R_w W_p I_j) \quad (4-39)$$

where:

F_p	=	unit contaminant wet plus dry deposition rate onto plant surfaces, $\text{pg/m}^2\text{-yr}$
C_p	=	air-borne particulate phase contaminant concentration, pg/m^3
V_d	=	deposition velocity, m/yr
I_j	=	fraction of particulates intercepted by crop j during deposition, unitless
RN	=	annual rainfall, m/yr
R_w	=	fraction of particles retained on vegetation after rainfall, unitless
W_p	=	volumetric washout factor for particulates, unitless

Following is brief guidance on assignment of values to the terms in Equations (4-35) to (4-39).

● **C_s and Kd_s :** This is the soil concentration and soil/water partition coefficient, respectively. The soil concentration is specified for the soil contamination source category. When the soil contamination is distinct from the site of exposure, the soil concentration at the site of exposure is modeled. As discussed in Section 4.3.2 above, two soil concentrations including one for a no-till and one for a tilled situation, are modeled in this situation. For modeling below ground vegetable concentration, the tilled concentration is required. The soil partition coefficient is a function of the contaminant organic carbon partition coefficient, Koc , and the soil organic carbon fraction, OC_{sl} , as discussed above in Section 4.3.1. Division of C_s by Kd_s results in the equilibrium soluble phase concentration of the contaminant, in mg/L .

● **RCF:** Briggs, et al. (1982) conducted experiments measuring the uptake of several compounds into barley roots from growth solution. He developed the following relationship for lipophilic compounds tested (lipophilic compounds were identified as those tested that had $\log Kow$ 2.0 and higher ($n=7$, $r=0.981$):

$$\log RCF = 0.77 \log (Kow) - 1.52 \quad (4-40)$$

where:

- RCF = root concentration factor equaling the ratio of the contaminant concentration in roots (fresh weight basis) and the concentration in soil water, unitless
- Kow = contaminant octanol water partition coefficient, unitless

Since the highest log Kow of the seven for which this relationship was derived is 4.6, and the lowest log Kow for the dioxin-like compounds is above 6.0, this relationship may not hold for the dioxin-like compounds. However, a validation exercise described in Chapter 7 where predictions of dioxin-like compounds in carrots are compared with observations shows this factor to adequately perform for this class of compounds.

Briggs' experiments were conducted in growth solution. Therefore, the RCF is most appropriately applied to soil water in field settings. This is why the C_s was divided by K_d in Equation (4-35).

- VG_{bg} : This correction factor and the one used to correct for air-to-leaf transfer of contaminants, VG_{ag} , are based on a similar hypothesis. That hypothesis for VG_{bg} is that the uptake of lipophilic compounds into the roots of this experiments is due to sorption onto root solids. High root concentrations were not due to translocation to within portions of the root hairs. Direct use of the RCF for estimating concentrations in bulky below ground vegetation would overestimate concentrations since available data suggests some but little translocation to inner parts of below ground bulky vegetation for the dioxin-like compounds. The experiments of Muller, et al. (1994) showed that the outer portions (peel) of carrots had higher concentrations of dioxin congener groups as compared to inner portions (cortex and stele). However, they also found concentrations within the carrot, suggesting some within plant translocation. Their data is examined below and used to assign a value for VG_{bg} in this assessment.

One set of important soil-to-plant transfer experiments, however, did suggest that certain plants would sorb and translocate dioxins to a significant extent. Hulster, et al. (1994) found that dioxins were sorbed by the roots of vegetables of the cucumber family and made their weight into the above ground portions of these plants. They were unable to explain why this happened and noted that it was a distinctly different trend than they found in several of their other soil-to-plant transfer experiments. For this assessment, it will be assumed that the vegetables of the cucumber family are an anomaly and not typical of vegetation for human or animal consumption.

VG_{bg} converts an outer portion, or skin, concentration, into a whole plant concentration. If inner portions were entirely free of residue, the correction factor could be estimated as the ratio of the mass of the outer portion to mass of the entire vegetable:

$$VG_{bg} = \frac{MASS_{skin}}{MASS_{vegetable}} \quad (4-41)$$

where:

VG_{bg}	=	below ground vegetation correction factor, unitless
$MASS_{skin}$	=	mass of a thin (skin) layer of below ground vegetables, kg/m ²
$MASS_{vegetable}$	=	mass of the entire vegetable, kg/m ²

Simplifying assumptions are now made to demonstrate this ratio for a carrot and a potato. First, it will be assumed that the density of the skin and of the vegetable as a whole are the same, so the above can become a skin to whole vegetable volume ratio. The thickness of the skin will be assumed to be same as the thickness of the barley root for which the RCF was developed. Without the barley root thickness in Briggs, et al. (1982), what will instead be assumed is that the skin thickness is equal to 0.03 cm. This was the thickness of a leaf from broad-leaved trees assumed by Riederer (1990) in modeling the atmospheric transfer of contaminants to trees. The shape of a carrot can be assumed to be a cone. The volume of a cone is given as $(\pi/3)r^2l$, where r is a radius of the base and l is length. Assuming a carrot base radius of 1 cm and a length of 15 cm, the volume is 16 cm³. The curved surface area of a cone is given as: $\pi r(r^2 + l^2)^{1/2}$, which equals 47 cm², given the r and l assumptions. The volume of the cone surface area is 47 cm² * 0.03 cm, or 1.41 cm³. The skin to whole plant ratio for this carrot is 0.09 (1.41/16). A similar exercise is done for a potato, assuming a spherical shape with a radius of 3 cm. The volume is given as $4/3\pi r^3$, or 113 cm³. The surface area of a sphere is $4\pi r^2$, or 113 cm², and the volume of this surface area is 3.39 cm³. The skin to whole plant ratio for the potato is 0.03.

This exercise indicates lower bounds for such an empirical parameter. For exposure assessments, other factors which reduce vegetative concentrations should also be considered. Additional reductions in concentration result from peeling, cooking, or cleaning, for example. Wipf, et al. (1982) found that 67% of unwashed carrot residues of 2,3,7,8-TCDD came out in wash water, and 29% was in the peels. A peeled, washed carrot correction factor might instead be, 0.09*0.04, or 0.004 (0.09 from above; 0.04 = 100% - 67% - 29%). A 96% reduction in the estimated VG_{bg} for the potato (the potato is cleaned and the skin is not eaten; additional

reductions possibly when cooking the potato) would equal 0.001. In a site-specific application, the type of vegetation, preparation, and so on, should be considered.

As mentioned above, the Muller, et al. (1994) data did show concentrations in the inner parts of the carrot. They presented concentrations for the cortex and stele, as well as the carrot peel. One interesting trend with this data is that the cortex and stele concentrations are virtually the same with both the control and the contaminated soil. Also, the cortex and stele concentrations for the control carrots are slightly lower, but essentially similar to the peel concentrations for the control group. The authors of this research observed a lack of change in cortex and stele concentrations from the control to the contaminated soil, but offered no explanation. This suggests that the empirical parameter VG_{bg} should not be a constant but should vary, being higher at lower soil concentrations. With a lack of data to develop an algorithm for a varying VG_{bg} , it remains a constant for this assessment.

This data was examined to estimate the VG_{bg} . As noted above, a lower bound assignment of VG_{bg} for the hypothetical carrot was 0.09, and for the potato, was 0.03. This means that if there were absolutely no within plant translocation of dioxin residues - all residues were only in the skin of the carrot and potato - than the VG_{bg} would be 0.09 and 0.03. Muller, et al. (1994) did not include whole carrot concentrations or the necessary information to calculate whole carrot concentrations accurately. Therefore, simple assumptions will be made to do such. It will be assumed that the whole carrot concentration is estimated as 1 part peel concentration, 7 parts cortex concentration, and 2 parts stele concentration. The VG_{bg} is calculated as the whole carrot concentration divided by the peel concentration. Using this procedure, it is found that the VG_{bg} for the control soil varied between 0.38 and 1.00 for the 10 congener groups, with an average of 0.60, and that it varied between 0.14 and 0.39 for the contaminated soil, with an average of 0.24. These estimates are obviously higher than 0.09, indicating, as the data shows, that within plant translocation does occur for carrots. This would suggest a VG_{bg} of between 0.24 and 0.60, absent any consideration of washing or peeling (actually the full range of 0.14 and 1.00, considering differences among congener groups).

Data was sought to do a similar exercise for potatoes. Hulster and Marschner (1991) present concentrations found in potato tubers, both peeled and unpeeled; no data for concentration in peels alone is presented. Like the Muller, et al. (1994) data, simple assumptions need to be made to estimate the peel concentration in order to estimate the VG_{bg} for this data set. As derived above, it will be assumed that the peel is 3% of the entire potato volume. With this assumption, VG_{bg} s of between 0.03 and 0.05 are calculated for potatoes from the data of Hulster and Marschner (1991). This suggests that, unlike carrots, much of the concentration in the

potato, even at low soil concentrations, resides in the peel. Like the carrot, some within plant translocation is indicated for potatoes.

Another difference between the carrot data in Muller et al. (1994) and the potato data in Hulster and Marscher (1991) is the potential impact of peeling. A ratio of whole vegetable to peeled vegetable was estimated for both these sets of data. For the Muller data on carrots grown in control soils, where the inner carrot concentrations were not substantially different than outer carrot concentrations, the estimated ratio was 0.91, meaning that peeling would not effect the full concentration in these carrots. It should be pointed out that the control soil Toxic Equivalent concentration, 5 ppt, is typical of soils that are considered “background” or “typical”. The impact of peeling was more pronounced for the contaminated soil, with an estimated ratio of 0.61. For the potatoes, peeling made a larger difference. The average peeled to unpeeled potato concentration ratio was about 0.20.

For the assessment in this document, “underground vegetables” are not any more defined than just that. Given the data examined in this section, a VG_{bg} of 0.25 will be assigned. This considers that a peeled carrot grown in typical soils could have a VG_{bg} of 0.60 according to the interpretation of the Muller, et al. (1994) data, whereas a peeled potato could have a VG_{bg} less than 0.01.

- C_v, C_p : The vapor (C_v) and particle (C_p) phase concentrations of contaminant in air, C_a , used in this algorithm is estimated using procedures described in Section 4.3.3 above.

- B_{vpa} : The first version of the air-to-leaf transfer factor used in the dioxin reassessment document (EPA, 1992b) used an empirical algorithm developed by Bacci and coworkers (Bacci, et al. 1990, 1992) who studied the vapor transfer of 14 organic chemicals, one of which was 1234-TCDD (not one of the 17 toxic congeners, but with similar fate properties to 2378-TCDD), to azalea leaves. These chamber experiments did not consider the effect of photodegradation on the transfer of the organic chemicals to the azalea leaves. The empirical relationship these researchers developed determined the volumetric transfer factor, B_{vol} , as a function of the contaminant Henry’s Constant and log Kow :

$$\log B_{vol} = 1.065 \log Kow - \log \left(\frac{H}{R_i T} \right) - 1.654 \quad (4-42)$$

where:

B_{vol}	=	Bacci volumetric air-to-leaf biotransfer factor, unitless [(μg contaminant/L of wet leaf)/(μg contaminant/L air)]
K_{ow}	=	contaminant octanol water partition coefficient, unitless
H	=	contaminant Henry's Constant, $\text{atm}\cdot\text{m}^3/\text{mol}$.
R_i	=	ideal gas constant, $8.205 \times 10^{-5} \text{ atm}\cdot\text{m}^3/\text{mol}\cdot\text{K}$
T	=	temperature, 298.1 K
-1.654	=	empirical constant

Then, McCrady and Maggard (1993) conducted chamber experiments on the transfer of 2378-TCDD vapors to grass leaves considering photodegradation. These experiments showed that the transfer of 2378-TCDD to grass leaves was about 40 times less than the transfer as calculated by the Bacci empirical algorithm. In addition to not considering photodegradation, McCrady and Maggard considered the difference in plant species between azalea leaves and grass leaves to be important in explaining the lower rate of transfer in their experiments as compared to Bacci's experiments. McCrady and Maggard's results were used in the next version of the air-to-plant model and the assignment of values to B_{vpa} (EPA, 1994). Specifically, the transfer factor for each dioxin congener was estimated using the Bacci algorithm, but this time all final results were divided by 40. Therefore, the B_{vpa} of the original model was reduced by a factor of 40 for all 17 dioxin and furan congeners for the second version of the air-to-leaf model.

Two key presumptions are inherent in using the Bacci algorithm divided by 40: 1) that the Bacci algorithm is generally appropriate for the dioxin congeners, despite the fact that the physical/chemical properties of the dioxin congeners are generally outside the range of the 14 organic chemicals used by Bacci, and 2) that the factor of 40 derived from one experiment on 2378-TCDD applies to all dioxin-like compounds.

The data of Welsh-Pausch, et al. (1995) will be used to develop an air-to-leaf transfer factor for the third version of the vapor phase air-to-leaf transfer factor described here, and also presented in Lorber (1995). Their data includes grass concentrations and air concentrations. Grass was grown in two flower boxes, with different agricultural soils in each box, beginning in May of 1991. The grass was cut back on July 17 in that year. On August 9, the grass was cut back again and the yield from the two boxes from the growth between July 17 and August 9 averaged $3900 \text{ g}/\text{m}^2$ fresh weight. This grass was analyzed for concentrations of dioxin congener groups, and these concentrations were provided on a fresh weight basis (i.e., pg/g fresh weight). On July 18, the first of two week long air samples were taken. These samples were taken very near the boxed grass. The samples were measured for the dioxin congener groups, not the

individual congeners. Representative congener group air concentrations were then determined as the average of the concentrations from the two samples. The concentration of dioxins in air remained relatively constant during the experimental period.

This data was used by McLachlan, et al. (1995) to verify an air-to-plant model based on fugacity concepts. Besides being a different model, McLachlan's modeling differed from the use of the data in this document in that it used to data to validate the model. Here, the data is used to calibrate a B_{vpa} . This was accomplished in the following 3-step procedure:

Step 1: Partition the total concentrations measured into a vapor and a particle phase.

McLachlan, et al. (1995) had used the glass fiber filter/XAD trap 2-stage high volume air samplers to estimate vapor and particle fractions from the total reservoir. This apparatus will yield "operationally defined" vapor and particle fractions. The vapor fraction estimated this way will be larger than the vapor fraction estimated using the Junge model as applied and described by Bidleman (1988). The Bidleman model will be used to partition the total air concentration of the Welsh-Pausch, et al. (1995) experiments into a vapor and a particle phase. Whether the Bidleman model is more "correct" than the measurements of the 2-stage sampler is an ongoing technical issue. A full discussion of the issue for dioxins can be found in Chapter 3. Also, model comparisons of predicted and observed vapor/particle partitioning for other organic contaminants, including PCBs, PAHs, and organochlorine pesticides can be found in Chapter 7. Table 4-3 shows the vapor/particle partitioning as developed using the Bidleman model and used here compared against the measured vapor/particle partitioning from the air sampling apparatus. As an example of how the measured and the modeled vapor fractions are different, the air sampling apparatus measures 72% of the PCDD congener group to be in the vapor phase, whereas the Bidleman approach estimates that 13% of the PCDD congener group is in the vapor phase.

The vapor and particle fractions for the congener groups are modeled assuming an air temperature of 20 °C, and a particle density in air corresponding to a condition which Bidleman described as "background plus local sources". The average air temperature between July 17 and August 9 of 1991 was 18 °C (McLachlan et al., 1995), and the "background plus local sources" designation also appears most appropriate for the university city of Bayreuth, described as a typical background situation for this area of Europe by Welsh-Pausch, et al. (1995). Two alternate options instead of background plus local sources appear less relevant for Bayreuth: an "urban" condition (higher particle densities) and a "background" condition (lower particle densities).

Step 2: Model the deposition of particle-bound dioxins to the grass, and subtract out the resulting modeled grass concentration from the total concentration. Since an air-to-leaf vapor phase transfer factor is sought in this exercise, what is needed is the grass concentration due only to vapor transfers. The particle-bound impact to vegetation cannot be measured directly. Therefore, a model will be applied to estimate that part of total grass concentration of dioxin that was due to particle bound depositions. The model that will be applied was described earlier and is shown in Equation (4-38).

Step 3: What is now available after accomplishment of the above two steps is a concentration of vapor phase dioxins in air and a concentration of dioxins in grass due to vapor phase transfers. With appropriate conversions, the air-to-leaf transfer factor is now simply calculated as the vapor-impacted grass concentration divided by the vapor phase air concentration.

As noted, Equation (4-38) is used to estimate the particle deposition impact to the grass. The deposition F can be estimated as the particle bound fraction times a deposition velocity. The velocity of deposition will be assumed to be 0.002 m/sec, which was the velocity of dry deposition of dioxins as measured by Koester and Hites (1992). Wet deposition was not considered for this brief exercise; McLachlan, et al. (1995) indicates that only a small amount of rain fell during this time and that results implied that rain washed off the grass leaves. The interception fraction will be assumed to be 0.59, based on information provided in Baes, et al. (1984). A first-order weathering rate of 0.0495 day^{-1} , corresponding to a 14-day half-life, is used in this model. The experiment occurred between July 17 and August 9, so a time t of 24 days is assumed. Assuming 15% dry matter in grass, the fresh weight yield of 3900 g/m^2 translates to a yield of 0.585 kg/m^2 dry. The final fresh weight concentrations due to particle depositions and vapor transfers are shown in Table 4-3.

Also shown in Table 4-3 in the last column is the percent of total plant concentration that is estimated to be due to vapor transfers. Except for the octa congeners, it would appear that the grass is mostly impacted by vapor transfers. This, of course, is contingent on the validity of the particle impact model.

The volumetric air-to-leaf transfer factor, referred to as B_{vol} , is defined as the volumetric concentration of dioxins in grass due to vapor phase transfers divided by the volumetric concentration of dioxins in air. Appropriate units expressing this ratio are: $[\text{pg dioxin/m}^3 \text{ grass}]/[\text{pg dioxin/m}^3 \text{ air}]$. The air concentrations are already in the appropriate units. The grass concentrations as given in Table 4-3 are in units of ng dioxins per kg plant fresh weight; these concentrations need to be converted into a volumetric basis. To do the conversion, the denominator in this grass concentration needs to be converted to a volumetric basis. McCrady

and Maggard (1993) use a volumetric factor of 0.77 kg fresh leaf/L volume. Two other conversions necessary are a conversion from L to m³ and a conversion from ng to pg. The final volumetric plant concentration in appropriate units is given as:

$$GC_{vol} \frac{pg \text{ dioxin}}{m^3 \text{ volume}} = GC_{fr} \frac{ng \text{ dioxin}}{kg \text{ plant fresh}} \frac{0.77 \text{ kg/L } 1000 \text{ pg/ng}}{0.001 \text{ m}^3/\text{L}} \quad (4-43)$$

where GC_{vol} is the volumetric grass concentration desired for calculation of B_{vol} , and GC_{fr} is the fresh grass concentration as reported in McLachlan, et al. (1995).

Table 4-4 now develops the final mass-based transfer factors, B_{vpa} . The volumetric transfer factor needs to be converted to the mass-based transfer factor, B_{vpa} :

$$B_{vpa} = \frac{1.19 \text{ kg/m}^3 B_{vol}}{0.15 \text{ 770 kg/m}^3} \quad (4-44)$$

The B_{vpa} developed here for congener groups will be applied to all congeners in the congener group. The B_{vpa} for the congener groups calculated in this manner are compared against the B_{vpa} as developed in an earlier version of the Dioxin Exposure Document (EPA, 1994) which, as described above, were developed as function of the Bacci algorithms with an empirical correction factor based on the experiments of McCrady and Maggard (1993).

The B_{vpa} as calculated with the data of Welsh-Pausch, et al. (1995), are lower than the B_{vpa} as calculated in the earlier Dioxin Exposure Document (EPA, 1994). For 7 of the 10 congener groups, the difference is less than an order of magnitude. The exceptions are the two octa congeners and the hepta dioxin congener, where the B_{vpa} calculated from the Welsh-Pausch, et. al (1995) data are two or more orders of magnitude lower for the octa congeners and 1 order of magnitude lower for the hepta dioxin congener. In general, the trend of increasing B_{vpa} from the tetra through the octa congeners is consistent with both approaches.

It may be informative to speculate on why the transfer of vapor phase dioxins appears to be lower in the Welsh-Pausch, et. al (1995) data as compared to the McCrady and Maggard (1993) data. There may be a relevant species difference, such as the lipid content for example, in the grass species used by McCrady and Maggard (1993), Reed canary grass (*Phalaris*

arundinacea L.), and the grass in the Welsh-Pausch, et al. (1995) experiments, Welsh Ray Grass (*Lolium multiflorum*). The climate might have different in Bayreuth, leading to more photodegradative loss in the Welsh-Pausch data. Certainly the experimental designs were different. McCrady and Maggard (1993) used a 2-stage chamber experimental design, including an uptake phase in which the grass was not exposed to sunlight, and a release phase where the grass was kept in sunlight. Uptake and release were occurring simultaneously and in sunlight in the Welsh-Pausch, et al. (1995) experiments. Certainly it seems possible that the net transfer rates might have been lower in the McCrady and Maggard (1993) experiments had the uptake and release phases both occurred in sunlight.

It should be noted that all bioconcentration or biotransfer parameters, such as the B_{vpa} , are qualified as second order defaults for purposes of general use. Section 6.2. of Chapter 6 discusses the use of parameter values selected for the demonstration scenarios, including a categorization of parameters. Second order defaults are defined there as parameters which are theoretical and not site specific, but whose values are uncertain in the published literature. The parameter values in this category should be considered carefully by users of the methodology. However, a model testing exercise published in Lorber and Pinsky (1999) and described in Chapter 7 lends credibility to the use of these CDD/F B_{vpa} for general purposes.

- VG_{ag} : The same discussion for this correction factor for below ground vegetation applies here. Fruits such as apples, pears, plums, figs, peaches, and so on, can be approximated by spheres, and upper bound estimates of correction factors would be less than 0.05. Peeling, cooking, and cleaning further reduces residues. The VG_{ag} for unspecified above ground fruits and vegetables in this assessment is assumed to be 0.01. Like VG_{bg} , this value is assigned considering that it should be less than estimated just based on surface volume to whole fruit volume ratios.

Two other VG_{ag} values are required for this assessment. One is for pasture grass and the other for other vegetation consumed by cattle. Both are required to estimate concentrations in these vegetation consumed by cattle in order to estimate beef and milk concentrations. A VG_{ag} value of 1.0 was used to estimate pasture grass concentrations since there is a direct analogy between the grass in the Welsh-Pausch, et al. (1995) experiments for which the B_{vpa} was developed and pasture grass of the cattle diet. However, VG should be less than the other general category of cattle vegetation defined in this assessment, "hay/silage/grain". Pasture grass is considered as a separate diet category because it is a principal component of the cattle diet and most subject to impact by dioxin-like compounds because it is leafy, whereas other cattle

vegetation are lumped together in this second category. As described below, this second general category of non-grass cattle vegetation include some thin leafy (hay) as well as bulky (corn silage and other grains) vegetation to consider. A volume ratio of outer surface to whole surface area to volume vegetation could be used to assign a value to VG, if specific assumptions concerning proportions of each type of vegetative cattle intake were made. An appropriate assumption for a fully protected vegetation such as grain would be zero. Silage can be considered part protected and part leafy. Since specific assumptions concerning hay/silage/grain intake are not being made for this exercise, a simple assumption that VG equals 0.50 for hay/silage/grain is instead made, without rigorous justification.

The only experimental evidence that a VG_{ag} for vapor transfers of dioxin-like compounds is justified came in a study by McCrady (1994). McCrady experimentally determined uptake rate constants, termed k_1 , for vapor phase 2,3,7,8-TCDD uptake into several vegetation including kale, grass, pepper, spruce needles, apple, tomato, and azalea leaves. Recall that the similar experimental design of both McCrady and Maggard (1993), and Bacci, et al. (1990; 1992), included an initial phase where vegetation in experimental chambers were exposed to the vapor-phase organic chemicals. The uptake which occurs during this initial phase is described with the rate constant, k_1 . A second "elimination" phase then occurs where organic vapors are removed from the chambers and the chemicals allowed to volatilize or otherwise dissipate from the vegetation. The rate constant for this phase is termed k_2 . A steady state bioconcentration factor (i.e., B_{vpa}), is then estimated as k_1/k_2 . The uptake rate constants from air to the whole vegetation estimated in the McCrady (1994) experiments demonstrate the concept behind the VG parameter. The uptake rate for an apple divided by the uptake rate for the grass leaf was 0.02 (where uptake rates were from air to whole vegetation on a dry weight basis). For the tomato and pepper, the same ratios were 0.03 and 0.08. The VG_{ag} is 0.01 for fruits and vegetables in this assessment, but note above that the simple exercise with a conical carrot and spherical potato estimated a surface volume to whole fruit volume ratio of 0.09 (carrot) to 0.03 (potato); a value of 0.01 for fruits and vegetable empirically considers factors such as washing or peeling which would reduce exposures. McCrady (1994) then went on to normalize his uptake rates on a surface area basis instead of a mass basis; i.e., air to vegetative surface area instead of air to vegetative mass. Then, the uptake rates were substantially more similar, with the ratio of the apple uptake rate to the grass being 1.6 instead of 0.02; i.e., the apple uptake rate was 1.6 times higher than that of grass, instead of 1/50 as much when estimated on an air to dry weight mass basis. The ratios for tomato and pepper were 1.2 and 2.2, respectively. McCrady (1994) concludes, "The results of our experiments have demonstrated that the exposed surface area of plant tissue is an important

consideration when estimating the uptake of 2,3,7,8-TCDD from airborne sources of vapor-phase 2,3,7,8-TCDD. The surface area to volume ratio (or surface area to fresh weight ratio) of different plant species can be used to normalize uptake rate constants for different plant species." McCrady cautions, however, that uptake rates are only part of the bioconcentration factor estimation, and he is unsure of the impact of surface area and volume differences on the elimination phase constant, k_2 (personal communication, J. McCrady, US EPA, ERL-Corvallis, Corvallis, OR 97333). Still, his experiments do appear to justify the use of a VG parameter since the B_{vpa} were developed on an air to whole plant mass basis, and his results are consistent with a VGag of 0.01 for fruits and vegetables.

● **kw:** Fries and Paustenbach (1990) note that this approach may overestimate concentrations because crops can be harvested or pastures grazed before the plant concentrations reach steady state, and that a kw based on a weathering half-life of 14 days may be too long given experimental results of Baes, et al. (1984) which showed a range of 2-34 days, and a median value of 10 days. On the other hand, Umlauf and McLachlan (1994) discuss the phenomena of the transfer of semivolatile organic compounds (SOCs) from depositing particles onto the leaf - the particles themselves may weather off the leaves with a half-life of 14 days, but the SOCs would transfer from the particle and not weather off the leaves. Umlauf and McLachlan (1994) could not find information on the transfer of SOCs from particles to leaves, but they speculated that the lipid covering of the cuticle would facilitate a rapid particle to leaf transfer. In their modeling of several SOCs to spruce leaves, they assumed that the SOCs completely transferred from the particles to the leaves in both wet and dry particle-bound deposition with no subsequent loss of contaminant via weathering or degradation. This is equivalent to assuming an infinite half-life rather than a 14-day half-life. Umlauf and McLachlan (1994) found reasonable model performance when comparing their modeling results with measurements of several SOCs including some PCBs on spruce leaves. Stevens and Gerbec (1988) used a 14-day half-life but did not assume a steady-state concentration is necessarily reached in vegetation. They considered harvest intervals by including the exponential term, $(1-e^{-kt})$, and assigning values of t based on harvest intervals of different crops. This assessment uses a kw of 18.02 yr^{-1} , which is equivalent to a half-life of 14 days. However, based on the discussions of Umlauf and McLachlan (1994), this is recognized as an important area of uncertainty. If their consideration of the transfer of SOCs from particles to leaves is valid, than an assignment of a kw of 18.02 yr^{-1} will significantly underestimate the impact of dry and wet deposition to vegetation.

● **I_j and Y_j:** Interception values and crop yields were determined in the aforementioned assessments based on geographic-specific crop yield data provided in Baes, et al., (1984) and the following types of crop-specific relationships estimating interception fraction based on yield (Y), also presented in Baes, et al., (1984):

$$\begin{aligned} \text{corn silage: } & I = 1 - e^{-0.768Y} \\ \text{hay/grasses: } & I = 1 - e^{-2.88Y} \\ \text{lettuce: } & I = 1 - e^{-0.068Y} \end{aligned}$$

Judgments by Fries and Paustenbach (1990) on high, medium, and low yields of silage, hay, and pasture grass, and the use of the first two interception equations above (the first for silage, and the second for hay and grass), can give some guidance on interception fractions and yields for these crops:

	Yield (kg/m ²)	Intercept Fraction
corn silage	0.30 (low)	0.20
	0.90 (med)	0.50
	1.35 (high)	0.64
hay	0.25 (low)	0.51
	0.45 (med)	0.73
	1.30 (high)	0.98
grass	0.05 (low)	0.13
	0.15 (med)	0.35
	0.35 (high)	0.64

This information can be used for cattle intake of vegetation, and the resulting beef and milk concentrations. The medium values for grass, 0.15 kg/m² yield and 0.35 interception, were used for the example setting in Chapter 5. An average of the medium values for hay and silage, 0.63 kg/m³ yield and 0.62 interception, were used for the second category of cattle vegetation for Chapter 5, the hay/silage/grain category.

Stevens and Gerbec (1988), using yields obtained from the Minnesota State Agricultural Office, derived the following yield and interception estimates, respectively, for vegetables for human consumption in their assessment: lettuce - 8.6,0.72; tomatoes - 12.0,0.55; and beans - 2.7,0.18. Average yields and interception fractions from their exercise: 7.8 kg/m² and 0.48, were used in the example setting in Chapter 5. These vegetable yields are fresh weight, so they need

to be converted to a dry weight basis in order to estimate a C_{ppa} appropriate for use in Equation (4-38). Since vegetables are generally 80 ->90% water, a fresh to dry weight conversion factor of 0.15 was used, resulting in an average vegetable dry matter yield of 1.17 ($7.8 * 0.15$). This was used in the example settings in Chapter 5.

- V_d : Particles settle to the ground surface and plant surfaces due to the forces of gravity. Gravitational settling velocity is a function of particle size, with more rapid settling occurring with larger particles. The algorithm used to estimate the concentration of contaminated particulates in air estimates the suspension of particles less than and equal to 10 μm , which is commonly referred to as inhalable size particles. Seinfeld (1986) listed a gravitational deposition velocity of 1 cm/sec for 10 μm size particles. This deposition velocity will be used in this assessment, and in units of m/yr, this equals 315,360 m/y.

- **RN**: Geraghty, et al. (1973) provides a map showing isolines average annual rainfall throughout the United States. This map shows low rates of 5 to 20 inches/year in the desert Southwest, moderate rates of 25 to 40 in/yr in the Midwest cornbelt, 40 to 60 in/yr in the South, and so on. The example scenarios of Chapter 5 were described as rural, with land in agricultural and non-agricultural settings. A rate of 1 m/yr (39 in/yr) will be used in the example scenarios.

- R_w : It is assumed that dry depositions fully adhere to plant surfaces; the weathering constant, k_w , models the loss of the vegetative reservoir of particle bound contaminants due to wind, rain, or other weathering process. However, it is not clear that wet deposition should also be assumed to fully adhere during a wet deposition event. Hence, the R_w parameter, or fraction of wet deposition adhering, was introduced. Prior modeling efforts of the impact of depositions of dioxin-like compounds to vegetation are unclear with regard to wet deposition. Stevens and Gerbec (1988), Fries and Paustenbach (1990), Webster and Connett (1990), and Travis and Hattemer-Frey (1991) all model particle deposition impacts of 2,3,7,8-TCDD to vegetation in air-to-beef/milk modeling. None of them discuss the distinction in wet and dry deposition, and model "total deposition" impacts, describing total as wet and dry deposition, total deposition, or simply as deposition. On the other hand, McKone and Ryan (1989) reduce the wet deposition portion of total deposition. They promote use of a "b", which they define as the fraction of material retained on vegetation from wet deposition. They recommend a value between 0.1 and 0.3.

The clearest indication of the fate of wet deposition of particles can be found in Hoffman, et al. (1992). In that field study, simulated rain containing soluble radionuclides and insoluble particles labeled with radionuclides was applied to pasture-type vegetation under conditions similar to those found during convective storms. The fraction of the labeled particles found to remain on the vegetation after the rainfall varied from 0.24 to 0.37. Nine values comprised this range, including particle sizes of 3, 9, and 25 μm , and cover described as clover, fescue, and mixed (a site with old field vegetation including fescue, grasses, weeds, and wild flowers). Based on this work, the R_w will be assumed to be 0.30 for all vegetation and dioxin congeners of this assessment.

● W_p : Washout ratios are generally defined as the concentration of contaminant in rain to the concentration of contaminant in air. Concentrations of contaminants in air and rain water can be derived as a mass of contaminant divided by a mass of air/water or a volume of air/water. Mackay, et al. (1986) shows that volume-based washout ratios (mass of contaminant mixing in m^3 air or water, e.g.) exceed mass-based washout ratios (mass of contaminant mixing in kg of air or water) by a factor of 815, which is the ratio of water and air densities. The washout ratio used in this assessment is a volumetric ratio based on methodologies described by Bidleman (1988). Using a volumetric ratio then allows for direct use of contaminant concentrations estimated in this methodology since they are already on a $\mu\text{g}/\text{m}^3$ volume basis.

Bidleman (1988) defines the overall washout ratio as: $(\text{mass contaminant}/\text{volume rain}) \div (\text{mass contaminant}/\text{volume air})$. Bidleman (1988) also discusses that fact that overall washout includes both wet deposition of particulates and scouring of contaminants in the vapor phase. He includes methodologies for estimating the vapor/particulate ratios for semi-volatile organic compounds (abbreviated SOCs) and also for estimating the washout ratios for vapors. However, he claims that if H is sufficiently high, vapor dissolution in droplets is negligible and only the particulate fraction is removed by wet deposition. He claims this to be the situation for n-alkanes, PCBs, chlordane, DDT, and 2,3,7,8-TCDD. Developing overall washout ratios for these and several other SOCs, he estimates that vapor scouring accounts for 1% of the overall washout ratio for 2,3,7,8-TCDD. For PCBs, he estimates similar percentages of 2, 4, and 28% for Aroclors 1260, 1254, and 1248, respectively. Based on this work, it will be assumed that vapor scouring of the dioxin-like compounds is small in comparison to wet deposition and the washout ratio for this assessment will only be applied to the air-borne particulate concentration of dioxin-like compounds.

Bidleman (1988) does not provide a chemical or site-specific equation which estimates the particle-phase washout ratio (which he does for the vapor-phase washout ratio). Rather, he summarizes available data and concludes that there is a wide range of the particle-phase washout ratio, W_p , for SOC: between 2×10^3 and 1×10^6 . He claims that a typical range is 10^5 to 10^6 , and uses a W_p of 2×10^5 in his exercises to estimate the overall washout ratio for several SOCs.

Koester and Hites (1992) list vapor and particle scavenging ratios for congener groups of dioxin-like compounds. To derive these ratios, they used air concentrations for congener groups that were taken at one time period in Bloomington and Indianapolis, Indiana, and rainfall depositions of these compounds at these sites measured during a second period of time. Using the Bidleman vapor/particle partitioning model used in this assessment, they estimate the vapor/split for the air concentrations. With these observations and models, they conclude that the overall washout ratio (sum of vapor and particle ratios) ranges from 10^4 to 10^5 , which contrasts the typical range of 10^5 to 10^6 noted above from Bidleman (1988). Also, their calculations indicate that vapor scavenging of dioxin-like compounds is comparable to particle scavenging, also in contrast to the Bidleman analysis summarized above. However, they did not state whether their washout ratios were volume or mass-based. If they were mass-based, then a conversion to volume based would put them in the 10^7 to 10^8 range, which seems improbable given the Bidleman summary above. Therefore, it will be assumed that they are volume-based, and they are appropriate to use for this assessment. Since no clear trend for particle washout ratios with regard to the degree of chlorination increased appears in Koester and Hites' data, the midpoint of their calculated range, 5×10^4 , will be used for all example compounds in this assessment.

As a final note, the multiplication of the above terms, $W_p * C_{pa} * RN * R_w$, does result in wet deposition in appropriate units of $\mu\text{g}/\text{m}^2\text{-yr}$, although that is not immediately obvious. First, multiplication of W_p , in $(\mu\text{g contaminant}/\text{m}^3 \text{ rain}) \div (\mu\text{g}/\text{m}^3 \text{ air})$, and C_{pa} , in $\mu\text{g contaminant}/\text{m}^3 \text{ air}$, leaves a partial term in units of $\mu\text{g contaminant}/\text{m}^3 \text{ rain}$. Then, multiplication of this partial term times annual rainfall rate, thought of as $\text{m}^3/\text{m}^2\text{-yr}$ instead of m/yr , gives the final quantity in the appropriate units.

When calculating concentrations in below ground fruit and vegetables using Equation (4-35), C_{bgv} is on a fresh weight basis since the RCF developed by Briggs, et al. (1982) is on a fresh weight basis, and no correction for estimating exposures is necessary. However, C_{abv} as estimated in Equation (4-36) is on a dry weight basis, and should be multiplied by a dry weight to fresh weight conversion factor when applied to above ground fruits and vegetables. A reasonable estimate for this parameter for fruits and vegetables is 0.15 (which assumes 85% water), which

was used in this assessment. When using Equation (4-36) to estimate C_{abv} for the beef and milk food chain algorithm, a conversion to fresh weight is not required, however, since the algorithms were developed assuming dry weight concentrations.

4.3.4.3. *Beef and Milk Concentrations*

The algorithm to estimate the concentration of contaminant in beef and/or milk was based on methods developed by Fries and Paustenbach (1990). They developed the beef bioconcentration factor for 2,3,7,8-TCDD, which is defined as the ratio of the concentration of the contaminant in beef fat to the concentration in the dry matter dietary intake of the beef cattle. They discussed bioavailability, which, as they define it, is the fraction of ingested contaminant which is absorbed into the body. It depends on the vehicle of ingestion - dioxin in corn oil has a bioavailability in the range of 0.7 to 0.8, in rodent feed it has an estimate of 0.5, while in soil it has a range of 0.3 to 0.4. They emphasized the importance of the differences in diet between cattle raised for beef and those which are lactating in explaining different food product concentrations. Although there is likely to be some difference in the bioconcentration tendencies for lactating and non-lactating cattle, Fries and Paustenbach in fact used the same bioconcentration for beef fat and milk fat, and the same will be done here.

The concentration in the fat of cattle products is given as:

$$C_{fat} = BCF FF (DF_s B_s AC_s + DF_g AC_g + DF_f AC_f) \quad (4-45)$$

where:

C_{fat}	=	concentration in beef fat or milk fat, pg/g
BCF	=	bioconcentration ratio of contaminant as determined from cattle vegetative intake (pasture grass or feed), unitless
FF	=	feedlot factor for beef fat calculation, ≤ 1 for beef fat and =1 for milk fat, unitless
DF_s	=	fraction of cattle diet that is soil, unitless
B_s	=	bioavailability of contaminant on the soil vehicle relative to the vegetative vehicle, unitless
AC_s	=	average contaminant soil concentration, pg/g
DF_g	=	fraction of cattle diet that is pasture grass, unitless
AC_g	=	average concentration of contaminant on pasture grass, pg/g

DF_f = fraction of cattle diet that is feed, unitless
 AC_f = average concentration of contaminant in feed, pg/g

The following is offered as brief guidance to these terms and also the justification for the values selected in the example Scenarios in Chapter 5.

● **Beef/milk bioconcentration factor, BCF:** Fries and Paustenbach (1990) developed the concept of a beef/milk bioconcentration ratio and applied it to 2,3,7,8-TCDD. BCF is defined as the concentration of contaminant in fat of cattle products (i.e., dairy and beef) divided by the concentration in dry matter intake. One key difference in the dietary intake of cattle raised for beef versus cattle raised for dairy is that cattle raised for beef tend to be pastured more than dairy cattle and be more exposed to contaminated soil, whereas lactating cattle are more often fed high quality feed, including grains which are expected to be substantially residue free since they are a protected vegetation. Another key difference is that the dioxins in lactating cows generally will reach a steady state in the fat of the animal (muscle fat and milk fat) much more rapidly than in non-lactating cattle because the excretion of milk will result in a large excretion of dioxins. For non-lactating cattle, excretion only occurs in feces and urine. Based on modeling, McLachlan (1994) speculates that it would take approximately 6 years for dioxins to reach steady state in non-lactating cattle because of the slow excretion rate through feces and urine, and that at steady state, concentrations in the muscle fat of non-lactating cattle would be much higher than in milk. However, dioxin concentrations in beef fat are generally found to be similar to that in milk fat. McLachlan (1994) explains it this way: "...it will take 6 yr to approach this steady state, much longer than the 1.5 yr that beef cattle typically live. During this time, the animal is also growing, continuously diluting its contaminant reservoir. As a result, the contaminant levels in commercial beef fat are generally not much higher than in milk fat." For this reason, the BCFs that are developed below based mostly on milk fat will be applied to both milk and beef fat.

Based on literature studies of cattle consuming feed contaminated with dioxin-like compounds, Fries and Paustenbach (1990) calculated a BCF of between 4 and 6, and assumed a value of 5.0 for 2,3,7,8-TCDD. Being developed directly from data of cattle ingesting contaminated feed, this BCF value of 5.0 already considers the bioavailability of the experimental contaminated feed. It will be assumed that the bioavailability of the cattle vegetation in this assessment equals that of the experimental feed. Therefore, a value of 5.0 can go directly into Equation (4-45) when applied to concentrations in grass and pasture. However,

this value should not be applied to soil, since it has been shown that TCDD on soil is less bioavailable than TCDD on other vehicles. This is why a B_s appears in Equation (4-45) - it adjusts BCF when applied to a soil concentration. The value of B_s is described below. The Fries and Paustenbach (1990) literature review is reproduced in Table 4-5, which additionally shows results generated based on information in McLachlan, et al. (1990) and Fries, et al. (1999).

Although the BCF of 5 determined by Fries and Paustenbach (1990) for 2,3,7,8-TCDD appears high based on the literature for this compound, Fries and Paustenbach (1990) discuss how short duration feeding trials (the 21 days of Jensen and Hummel (1982) and the 28 days of Jensen, et al. (1981)) do not result in steady state bioconcentration ratios. Extrapolating the data to a point where steady state is speculated to be reached, Fries and Paustenbach (1990) developed the arguments for the range of 4 to 6 for 2,3,7,8-TCDD. The second example compound in Chapter 5 was 2,3,4,7,8-PCDF. Fries and Paustenbach (1990) observed that bioconcentration ratios for PCDDs and PCDFs decreased significantly as chlorination increased, although their literature seems to imply that this effect is most pronounced for hepta- and octa- PCDDs and PCDFs. They could not locate data in the literature for penta-PCDDs or PCDFs.

McLachlan, et al. (1990) was the first study where BCFs for cow milk could be generated for furan congeners. They conducted a mass balance of dioxin and furan congeners in a lactating cow. They carefully accounted for 16 of the 17 dioxin and furan congeners of toxicity equivalency to 2,3,7,8-TCDD in the intake of a lactating cow in food, air, and water, and measured amounts in feces, urine, and milk, while attributing the rest of the intake to a compartment they termed, storage/degradation/experimental error. They obtained data well into steady state, and provided information necessary to estimate milk BCFs including: information appropriate to estimate the dry matter intake by the cattle; ng/day congeners in feed, water, and air; L/day milk production (density assumed to be 0.9 g/cm³); and percent fat in milk. The data for estimating the dry matter intake of the cattle was expressed in two ways. One, the wet weight of feed materials was given, and assuming a dry weight fraction (the actual dry weight fraction was not given), one could estimate a dry matter intake. Two, it was stated that the feces flux of 5 kg/day was 30% of the dry weight intake. Therefore, the dry matter intake is calculated at 16.7 kg/day. However, in a later report on this same data set (McLachlan, 1993), it was stated that the feces flux from this experimental animal of 7 kg/day was 33% of dry matter intake. In a personal communication (letter, M. McLachlan to M. Lorber dated 4/2/95), the author confirmed that the correct total dry matter intake was 21 kg/day, and this value was used in the generation of BCFs shown in Table 4-5.

Fries, et al. (1999) conducted a feeding experiment where four cows were fed PCP-contaminated wood. Specifically, a 3 g/day dose of ground PCP-treated wood was administered to each cow for 58 days. The mixed feed was sampled, and a sample of each cow's milk was obtained on days 28, 42, and 56. Feed amounts were carefully controlled to not only these cows but to other cows at the USDA agricultural research facility. Bulk milk was obtained from cows who were not treated, and the concentrations from these samples served not only as controls for the laboratory, but also were used to calculate a limited set of BCFs for background settings. BCFs were calculated when both feed and milk were higher than background. The results for the cows fed the wood as well as for background cows are shown in Table 4-5. As seen, there is reasonable agreement between the cows fed the contaminated wood and the background cows, with the exception, perhaps, of two of the furan congeners, and there is also good agreement between these BCFs and those developed from the data of McLachlan, et al. (1990). Also, the BCF for 2,3,7,8-TCDD was highest in this experiment at 7.1 as compared to other BCFs calculated for 2,3,7,8-TCDD

The McLachlan data will be used to assign BCFs for the demonstrations in Chapter 5. The BCF value for 2,3,7,8-TCDD value is 5.73 and the BCF for 2,3,4,7,8-PCDF is 4.13, in the demonstration scenarios which include a dioxin, a furan, and a PCB. For the demonstration of the incinerator, the suite of dioxin-like compounds are demonstrated, and the full BCF set developed by McLachlan and coworkers will be used.

A review of the literature for PCBs is given in Table 4-6. McLachlan and coworkers measured a suite of PCBs in his lactating cow mass balance experiments and reported the results in McLachlan (1993). However, unlike the dioxin results which showed a favorable mass balance result (i.e., most of the mass of the dioxin intake by the cow could be accounted for in the feces, urine, and milk - the remainder attributed to storage, metabolism, or experimental error), the PCBs results showed that up to 40% more PCBs were being excreted through urine, feces, and milk, than was taken up by the cattle. McLachlan (1993) discounted the possibility that the cow was losing body fat which could explain the result, and instead speculated that there was secondary contamination of the feed through binder twine that had been treated with recycled oil (i.e., the amount of PCB intake by the cow was underestimated). In any case, this data could not be used to generate BCFs for PCBs.

Although PCBs, dioxins, and furans are related compounds in terms of environmental fate characteristics, a difference in bioaccumulation potential is noted with higher degrees of chlorination, based on the study of Tuinstra, et al. (1981). Their work implies increasing bioaccumulation potential as the degree of chlorination increases. They developed BCF values

(defined in the same manner as in this assessment) for a suite of congeners identified to occur in Aroclor 1260 administered to lactating cows. Therefore, their data allowed for a partial examination on congener bioaccumulation patterns. The results given in Table 4-6 are interpreted from the data supplied in Tuinstra, et al. (1981). Tuinstra determined the identity and percentage of specific congeners which comprise Aroclor 1260. He was able to identify 36 congeners, but could only quantify 27 of them (because of the unavailability of standards for 9 congeners). These 27 comprised 81%, by mass, of the Aroclor 1260. Tuinstra was able to estimate BCF values for most, but not all, of the identified congeners - for 23 of the 27 congeners they identified (which equaled 77% of the congeners, by mass, of Aroclor 1260). As seen in Table 4-6, the average congener-group BCF value increases from about 2 to 4 going from hexa- to nanochloro-PCBs. However, there was a wide range of measured BCF values for specific congeners. In the heptagroup, for example, Tuinstra estimated BCF values between 0.4 and 5.2. Fries, et al. (1973) showed increasing BCF values in milk fat at 20, 40, and 60 days for Aroclor 1254 up to a value of 4.8 at day 60. The body fat BCF value at 60 days, the only time such a measurement was taken, was 3.4. The trend of having a higher BCF value for milk fat as compared to body fat for lactating cows was also noted by Willett, et al. (1987). They fed lactating cattle Aroclor 1254 sorbed to ground corn. In three sequential periods of 60 days, they fed the cattle 10, 100, and then 1000 mg/day of Aroclor 1254. Given their average daily dry matter intake of 19.5 kg during the experiment, the concentration during each of those 3 periods was 0.51, 5.13, and 51.28 mg/kg (ppm). However, milk and body fat concentrations of PCBs were given after 60, 120, and 180 days, so that for estimation of the BCF value, what is needed is average concentration of Aroclor intake after these periods. These averages are 0.51, 2.82, and 18.97 mg/kg. Given the reported concentrations of PCBs in milk and body fat after these experimental periods, BCF values were estimated and given in Table 4-6. Two studies, that of Willett and Liu (1982) and Perry, et al. (1981), contained data from which estimates of BCF could be made, except that these studies did not report daily dry matter intake. An estimate of 19.5 kg/day was assumed for lactating cattle for these studies, which was the experimental dry matter intake noted by Willett, et al. (1987). Willett and Liu (1982) dosed cattle for only 20 days, and arrived at the lowest noted BCF value for Aroclor 1254, 1.2. The trend of increasing BCF value over time of dosing was noted by Fries, et al. (1973). Willett, et al. (1990) conclude that steady state is reached after about 60 days, so that estimates of BCF made from experiments less than 60 days may not reflect steady state conditions. Perry, et al. (1981) had a high BCF value, 4.2, despite the dosing period being only 32 days. This would appear to be the result of having a high concentration in the diet. Similarly high BCF values with corresponding high

concentration in dosed intake were noted in Fries, et al. (1973) and Willett, et al. (1987). It should be noted that the concentrations in body fat in the studies of Willett and Liu (1982) and Perry, et al. (1981) were corrected as recommended by Willett, et al. (1990) in estimating BCF values.

Five trends for PCBs were discussed above: 1) that steady state is reached after approximately 60 days, 2) that higher BCF values appear to result with higher concentrations in feed, 3) that BCF values for milk fat may exceed those of body fat for lactating cows (this also seems true for dioxins/furans; see Table 4-5), 4) that the BCF values tend to increase with increasing chlorination of PCB congener groups, and 5) that this fourth trend is based on a limited set of data and much variability exists within specific congener groups.

Generally there is a sparsity and inconsistency in the data which would allow for definitive estimation of BCF values for the example heptachloro-PCB example compound in Chapter 5, 2,3,3',4,4',5,5'-PCB. Most of the data noted is for Aroclor 1254, and this data implies BCF values between 1.2 and 4.8. Based on the results from Tuinstra, et al. (1981) for the average of eight heptachloro-PCBs, a BCF value of 2.3 will be assigned to 2,3,3',4,4',5,5'-PCB.

It should be noted that all bioconcentration or biotransfer parameters, such as the BCF, are qualified as second order defaults for purposes of general use. Section 6.2. of Chapter 6 discusses the use of parameter values selected for the demonstration scenarios, including a categorization of parameters. Second order defaults are defined there as parameters which are theoretical and not site specific, but whose values are uncertain in the published literature. The parameter values in this category should be considered carefully by users of the methodology.

● **FF:** Fries and Paustenbach (1990) summarize pertinent literature to conclude that cattle raised for beef are not slaughtered without an intervening period of high-level grain feeding. Agricultural statistics (USDA, 1992) show that 32.9 million cattle were slaughtered in 1991. Of this number, 6.1 million were cows and bulls that likely did not go through a feedlot prior to slaughter. Quarterly statistics from 1991 show that at any time, cattle and calves on feed for slaughter range from 10 to 12 million. Fries uses these statistics to conclude that 75 to 80% of the total beef supply is from animals that went through a feedlot finishing process, and that the portion of beef that did not go through a feedlot process are (generally speaking) those 6.1 million cows and bulls (personal communication, G. Fries, USDA Agricultural Research Service, Beltsville, Maryland, 20705). He suggests that a representative feedlot finishing process would include a length of 120 days and diet consisting of 20% corn silage and 80% grain. The grains can be assumed to be residue-free, since grains are protected and, as discussed above, little

within plant translocation of outer contamination can be assumed. Also, the ears of the corn silage are in the same category, leaving only the stalks and leaves of the corn silage impacted by atmospheric transfers of dioxin-like compounds.

A feedlot finishing process is important to consider if assessing beef impacts in a site-specific assessment. However, data could not be found in the literature which measured the impact of this process to beef concentrations. Such impacts could occur as the result of increased weight gain from substantially residue-free feeds. Fries and Paustenbach (1990) and Stevens and Gerbec (1988) modeled the impact of a residue-free grain-only diet for four months prior to slaughter. Based on within-cow dilution and depuration considerations, both efforts estimated that the feedlot process would reduce beef concentrations by about one-half. This translates to an assignment of 0.5 for FF. This was the assumption used in the air-to-beef food chain validation exercise described in Chapter 7.

The demonstration scenarios of Chapter 5 assume that farming families slaughter a portion of their cattle for home consumption, and that they do not put their cattle through any special diet before slaughter. Therefore, an FF = 1 is assumed for the demonstration scenarios in Chapter 5.

With the use of an FF, it is noted that the quantity in the parenthetical of Equation (4-45) above describes the cattle diet prior to slaughter.

● **Soil bioavailability, B_s :** This parameter reduces the bioconcentration ratio, F, considering that soil is a less efficient vehicle of transfer compared to feed. Remember that the values of BCF appropriate for Equation (4-45) already consider bioavailability and were developed from experimental data placing the BCF of 2,3,7,8-TCDD in the 4 to 6 range. Fries and Paustenbach (1990) reviewed several studies on the oral bioavailability of TCDD in soil in the diet of rats, and concluded that soil is a less efficient vehicle of transfer as compared to rat feed. If the same is true for cattle - that soil is less efficient than their feed - than the BCF value must be reduced when applied to soil ingestion. Most studies reviewed by Fries and Paustenbach used corn oil as the positive control, since there is a high absorption of TCDD in rats when corn oil is used as the vehicle, with 70-83% of the administered TCDD dose absorbed. Their literature review on rat data showed that the bioavailability of TCDD in soil was between 0.4 and 0.5 that in corn oil, or 0.3 to 0.4 overall. The literature implied a range of 0.5 to 0.6 of TCDD in standard rat feed is absorbed, and although few studies were available, a similar 50% absorption rate of TCDD in cattle feed was noted. They concluded, therefore, that the rat data was a reasonable surrogate for cattle. The B_s can be thought of as the ratio of BCF values between soil

and feed, or, $(BCF_{soil})/(BCF_{feed})$. If the difference in BCF_{soil} and BCF_{feed} is explained solely by bioavailability differences, then the ratio of overall bioavailability of soil to feed should equal this ratio. As described above for rat data, the overall bioavailability of soil was 0.3-0.4, and the overall bioavailability of feed was 0.5-0.6. The ratio of overall bioavailabilities is, therefore, $(0.3-0.4)/(0.5-0.6)$. If the argument that this ratio equals the ratio of BCFs is valid, then this would lead to a B_s of 0.5 to 0.8. This implies that absorption of TCDD when soil is the vehicle is 50 to 80% of what it would be if feed were the vehicle. These assumptions and implications are made for this assessment, and the soil bioavailability term, B_s , used for all example compounds in Chapter 5 is 0.65.

- **Soil diet fraction, DF_s :** Fries and Paustenbach (1990) report that soil intake by cattle feeding on pasture varies between 2 and 18% of total dry matter intake, depending on whether the grazing area is lush or not. The soil diet fraction would be lower for cattle which are barn-fed with minimal opportunity for contaminated soil intake. Cattle raised for milk are rarely pastured, so one possible assumption for estimating milk fat concentrations would be a DF_s of 0.0. Fries and Paustenbach (1990) assumed between 0 and 2% of the dry matter intake by lactating cattle was soil in various sensitivity tests. Since cattle raised for beef are commonly pastured, a conservative assumption would be a high DF_s of 0.15 (15%), although a more reasonable assumption which would consider grazing in lush conditions and/or a portion of diet in feed or supplemental feed leads to DF_s less than 0.10. Fries and Paustenbach (1990) assumed DF_s of between 0 and 0.08 for beef cattle in various sensitivity tests. The example settings in Chapter 5 assume 0.02 (2%) for lactating cattle, and 0.04 (4%) for beef cattle.

- **Feed and grass diet fractions, DF_f and DF_g :** The sum of the three diet fractions, $DF_s + DF_f + DF_g$ must equal 1.0. Setting DF_s equal to 0.02 (2%) for lactating cattle assumed that they are pastured to some extent or could be taking in residues of soil sticking to home grown feed. Assuming lactating cattle graze a small amount of time, the DF_g for lactating cattle will be 0.08 (8%). This assessment simplifies the definitions of dairy and beef cattle diets by defining non-pasture grass vegetation simply as "feed". Feeds include hay, silage, grain, or other supplements. While dairy cattle are lactating, 90% of their dietary intake is assumed to be in this general category. Beef cattle spend a significant amount of time pasturing. However, their diet is supplemented with hays, silages, and grains, and particularly so in colder climates where they need to be housed during the winter. In this assessment, the simple assumption that

they ingest equal proportions of pasture grass and feeds is made. Therefore, with 4% soil ingestion, DF_f and DF_g are both 48% for beef cattle.

- **Average contaminant soil concentration, AC_s :** The simplest assumption for AC_s would be that it equals the initial level of contamination, C_s . However, this would be too high if the cattle also graze in uncontaminated areas. Where cattle have random access to all portions of a grazing area with contaminated and uncontaminated portions, a ratio of the spatial average of the contaminated area to the total area should be multiplied by C_s to estimate AC_s . If cattle spend more time in certain areas, these areas should be weighted proportionally higher. Different assumptions for determining AC_s might also be in order when using Equation (4-45) to estimate milk fat as compared to beef fat concentrations. Lactating cattle, if pastured, might graze on different areas than beef cattle. After determining a spatial average based on current conditions, a second consideration might be given to temporal changes. If soil levels are expected to change over time (due to changes in source strength or other factors) then the concentrations should be averaged over the exposure duration as well. The example scenarios in Chapter 5 where beef and milk exposures were estimated were termed "farms". The methodologies in this chapter were used to estimate the average soil concentration over the entire farm property. Assuming the cattle are raised on the farm property, than 100% of their intake of soil comes from the farm. This means that the average soil concentration, AC_s in Equation (4-45), is equal to the level of contamination given as the initial level, or determined as average for the farm based on fate and transport algorithms.

- **Average feed and pasture grass concentration, AC_f and AC_g :** The concentration of contaminant in pasture grass or feed is equal to C_{abv} as calculated in Equation (4-36). As described earlier, pasture grass or feed grown on-site can be impacted by air-to-plant vapor phase transfer and particulate deposition. Refinements noted above include the empirical parameter VG_{ag} equals 1.00 when applying the air-to-leaf transfer algorithm to pasture grass and 0.50 when applied to cattle feed. A refinement noted here, and like AC_s above, is that an assumption needs to be made about the fraction of feed or fraction of pasture grass that is impacted by contamination. Part of the feed diet could come from outside sources and not be contaminated, and part of the grazing area could be far from a localized area of soil contamination, making it less impacted by contaminated particulates or vapors. The simplest assumption is that the entire vegetative diet of the cattle includes pasture grass and feed impacted by the contaminated soil, in which case AC_f and AC_g would equal C_{abv} . For the sake of

simplicity and consistency, the assumption made for AC_s was also made for AC_f and AC_g in the example Scenarios in Chapter 5. That is, the grass and feed intakes of beef and dairy cattle originate within the farm property and concentrations in grass and feed are a function of the soil concentrations within the farm property; AC_f and AC_g are equal to C_{abv} as calculated in Equation (4-36). For site-specific situations, AC_f and AC_g should be estimated as C_{abv} reduced according to assumptions on quality of cattle feed, and impacts of air-borne contaminants on grazing land and cattle feed grown at the site where cattle are raised.

There is one final but critical note on solving for beef and milk concentrations given a solution for C_{fat} as in Equation (4-45). Human daily ingestion amounts are typically expressed in whole product rather than the fat portion of product. Whole milk is 4% fat, meaning that the C_{fat} needs to be multiplied by 0.04 to get whole milk concentration. Similarly, beef is generally 18-22% fat, meaning that the C_{fat} needs to be multiplied by 0.18-0.22 to get whole beef concentration. However, the ingestion rates in this assessment for beef and milk were developed on a fat basis, so no adjustment is necessary.

4.3.4.4. *Chicken and Egg Concentrations*

The algorithm to estimate the concentration of contaminant in chicken and/or eggs is the same algorithm as in beef/milk above. The experiments used to develop the chicken and egg bioconcentration factors were conducted by the Hazardous Materials Laboratory at the California EPA (Stephens, et al. 1995), and they will be described below. To review, the equation used to calculate the concentration of dioxin-like compounds in chicken and egg fat is:

$$C'_{fat} = (BCF DF_s B_s AC_s) + (BCF DF_g AC_g) + (BCF DF_f AC_f) \quad (4-46)$$

where:

- C_{fat} = concentration in chicken fat or egg fat, pg/g
- BCF = bioconcentration ratio of contaminant developed for chicken vegetative intake, unitless
- DF_s = fraction of chicken diet that is soil, unitless
- B_s = bioavailability of contaminant on the soil vehicle relative to the vegetative vehicle, unitless

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AC_s	=	average contaminant soil concentration, pg/g
DF_g	=	fraction of chicken diet that is incidental vegetation while free ranging, unitless
AC_g	=	average concentration of contaminant on free range vegetation, pg/g
DF_f	=	fraction of chicken diet that is feed, unitless
AC_f	=	average concentration of contaminant in feed, pg/g.

The scenario of principal concern for chicken and egg contamination is the free range chicken scenario. This is the scenario where chickens are allowed to graze during all, or a portion, of their lives. The feed they consume could be spread out on the ground or in troughs. When they are free ranging but not eating their formulated feed from troughs, they still may forage for vegetation or earthworms which would give them considerable exposure to soil and vegetation, not to mention the earthworms which could be a source of dioxin-like compounds (earthworm exposure is not considered in this model). The percentage of all chickens raised for meat or eggs in this manner is a very small percentage of the total; most chickens are raised in commercial settings where their cages are raised and they have little exposure to soil or vegetation. When raised this way, their exposure to dioxins is only through the feed, and measurements of dioxin in chicken feed have shown little or no dioxin residues (Chang, et al, 1989; Stephens, et al, 1995). Chang, et al. (1989) sampled eggs from three sources: from foraging chickens that were raised near a contaminated PCP site in Oroville, CA (see the discussion of BCF below for a discussion of this site), from foraging chickens that were raised 4.5 km away in the neighboring town of Palermo, and from a grocery store, which were considered the control eggs. They found that the eggs from the foraging chickens near the site contained the highest concentrations of dioxin and furan congener groups (individual congeners were not reported in Chang, et al., 1989), with eggs from Palermo containing concentrations of dioxins and furans about 3 to 5 times less, and the commercial eggs being one to two orders of magnitude less than the eggs from near the PCP site.

The demonstration of this pathway in Chapter 5 is a free range scenario. The following is offered as brief guidance to the parameters in Equation (4-46) above and also the justification for the values selected in the example Scenarios in Chapter 5.

● **Chicken/egg bioconcentration factor, BCF:** In 1987, an explosion and resulting fire occurred at the Koppers Wood Preservative Treatment plant in Oroville, CA. Subsequent environmental studies found soil concentrations of the tetra through octa congener groups up to the ppm level adjacent to the fire site, and impacts to foraging chickens were also found, as was

discussed above (Chang, et al, 1989). The concern over this site led Stephens, Petreas, Hayward, and colleagues at the Hazardous Materials Laboratory (HML) of the California Environmental Protection Agency (Cal-EPA) to begin an investigation to test the hypothesis that grazing chickens would bioaccumulate dioxins. The first phase of their study, the laboratory phase, involved dosing chickens with feed mixed with soils of varying known levels of dioxins and furans. The completed results of this study have been published (Stephens, et al. 1995), with earlier publications available on the design and some interim results (Stephens, et al., 1992; Petreas, et al., 1991). Briefly, the study design was as follows. White Leghorn (Babcock D 300) chickens were randomly assigned to three groups with 22 individual chickens per group. The control group was fed a formulated laying-bird diet containing 10% uncontaminated soil - i.e., soil from a rural background setting with low levels of dioxins and furans. The TEQ concentration on this uncontaminated soil was less than 0.5 ppt. The “low” group was fed the same formulated diet to which they mixed soil to obtain a 9 (feed):1 (soil) ratio. The decision to have soil be 10% of the diet was based on discussions they had with agricultural experts on the amount of soil a free range chicken would take in. The soil had a CDD/F concentration of 42 ppt I-TEQ. It was taken from the backyard of a residence near the Koppers site, and had a similar sandy loam texture as the uncontaminated soil. The “high” group was fed the same formulated diet containing 10% of the same backyard soil but this time with several of congeners spiked in the soil to much higher levels. The concentration on this spiked soil rose to 459 ppt I-TEQ. Analysis by Stephens, et al. (1995) suggested that this spiking did not affect the bioavailability of the spiked congeners in the soil. Analysis of the feed before the introduction of any soils showed non-detects (with detection limits near or below 1 ppt, mostly at 0.1 ppt) for all congeners. Once the soils and feed were mixed, the I-TEQ concentrations in the feed/soil mixture for the “control”, “low”, and “high” groups were 0.6, 3.2, and 35.8 ppt, respectively (counting non-detects at half-detection). Eggs were collected every 5 days during the first month and every 10 days thereafter. Chickens were culled on days 10, 20, 41, 80, 164, 188, 210 and 278. Samples were taken of blood, feces, liver, adipose, and thigh muscle. Stephens, et al. (1995) reported on the analysis of liver, adipose, thigh muscle and egg for the suite of 17 dioxin-like compounds at various time intervals.

They also developed bioconcentration factors for these four tissues and for both feeding regimes, “low” and “high”. To calculate the BCF, they averaged the tissue concentrations for days 80 and 164 when the animals had apparently reached a steady state, and for eggs at days 80, 160, and 178. The same will be done for the calculation of BCFs in this assessment. However, the BCFs for this assessment will be different than those published by Stephens, et al. (1995).

Their BCFs were defined as the concentration in the whole tissue on a wet weight basis divided by the concentration in the feed/soil mixture. Furthermore, although the concentration in the soil/feed mixture was determined and reported, Stephens, et al. (1995) surmised that the concentrations in the soil alone were more reliable than the concentrations measured in the feed/soil mixture. Therefore, the concentrations to which the chickens were exposed was calculated as the soil concentration divided by 10. The difference for this assessment is that the BCFs will be defined as the concentration in the tissue on a lipid basis divided by the concentration in soil, rather than the feed/soil mixture. The calculation for BCFs will also involve the use of the soil bioavailability term, B_s , as shown above in Equation (4-46). The procedure to calculate BCFs from the data is now explained.

Assuming that the chickens were not exposed to vegetation and that the feed concentrations were equal to 0.0 in the Cal-EPA experiments, Equation (4-46) reduces to the following:

$$C_{fat} = BCF DF_s B_s AC_s \quad (4-47)$$

The congener-specific BCFs were then easily calculated assuming that the DF_s is equal to 0.10 and, the B_s is equal to 0.65, as it was above for the beef/milk bioconcentration algorithm, and directly using the soil concentrations as reported in Stephens, et al. (1995). Table 4-7 shows the final BCFs calculated in this manner from the Cal-EPA data. Stephens, et al. (1995) made the following three pertinent observations regarding this data and the development of the BCFs: 1) the highest concentrations were found in the liver, implying that mechanisms other than lipid solubility operate in that organ, 2) the soil had a high organic matter content, which the authors suggested would result in a lower observed bioavailability of the dioxins in the chickens than could have been observed had the soil organic matter content been lower and perhaps more typical of agricultural soils, and 3) the BCFs were higher in the “high” exposure group as compared to the “low” exposure group.

With regard to the first observation, the higher BCFs for the liver as compared to the other three tissues is apparent from Table 4-7 for both the low and high group. This is not relevant for exposure unless, of course, one were predicting concentrations in chicken livers for human consumption. In that case, one could use the liver-specific BCFs in Table 4-7. With regard to the second observation, this is important in that it provides some justification for the B_s of Equation (4-47) which was assigned a value of 0.65. The BCFs in Table 4-7 should, therefore,

be interpreted as BCFs specific to non-soil chicken intakes which are assumed to include chicken feeds and incidental vegetation in the model used in this assessment. This makes the chicken/egg BCFs analogous to the beef/milk BCFs. With regard to the third observation, Stephens, et al. (1995) tested the observation statistically and found that the BCFs of 3 congeners - 12378-PCDD, 234678-HxCDF, and 1234678-HpCDF - were significantly different at the $p < 0.05$ level and that the BCFs of 2 congeners - 2378-TCDF and 1234789-HpCDF - were significantly different at the $p < 0.025$ level. Even without statistical significance, it does appear that the trend of higher BCFs for the high exposure regime holds up for the other congeners as well.

Other interesting trends to observe in this data qualitatively (without statistical rigor) are related to the bioconcentration differences between adipose, thigh, and egg within the low group alone and/or compared against the high group. One important observation is that, in the low group, the dioxins concentrate more in the adipose lipid as compared to the thigh lipid, but this difference is much smaller in the high group. This might suggest that the dioxins deposit first, or preferentially, in adipose tissue rather than muscle tissue at low doses. Another trend is that, at the low dose, the dioxins concentrate in the lipid of the thigh and the egg about equally, but in the high group, the dioxins concentrate more in the thigh lipid as compared to the egg lipid.

In real world settings, soil concentrations to which chickens are exposed are expected to be more like the “low” exposure as compared the “high” exposure. Because of this, the BCFs for the low exposure group will be used in this assessment. For site-specific assessments where the soils are highly contaminated, and the assessor has justification for assuming that chickens are grazing on the highly contaminated soil, it would be appropriate to use the BCFs for the “high” group. The BCFs developed for the thigh and egg will be used for the calculation of concentrations in chicken meat and eggs, respectively. This is a different strategy than for the calculation of dioxin concentrations in beef or milk. There, a single set of BCFs were used to calculate concentrations in the fat of beef or milk. Here, the data appears robust enough to support separate BCFs. BCFs for two congeners in the low group could not be reliably calculated because one or both of the measurements (i.e., the soil/feed measurement and/or the tissue measurement) were below the quantification limit. These congeners are 2378-TCDD and 234678-HxCDF. For 2378-TCDD, it is noted that for the high exposure group, the 2378-TCDD BCF is about 1.3 times that of the 12378-PCDD BCF for both the thigh and egg. Based on this observation, the BCF for 2378-TCDD for thigh and egg will be 8.8 (i.e., 6.8×1.3) and 7.8 (6.0×1.3), respectively. The BCFs for the three HxCDFs for which a BCF could be estimated appear to be within a factor of 2-3 of each other. Based on this observation, the BCF for 234789-HxCDF for the thigh and egg will be estimated as an average for the three HxCDFs for these

tissues for which the BCF was derived. This calculation results in a 234789-HxCDF BCF of 4.1 for thigh and 6.2 for egg.

The only data that could be found for developing PCB BCFs was from a study by Fries, et al. (1977), and this data was only pertinent for Aroclor mixtures. Fries, et al. (1977) fed caged White Leghorn hens, 41 weeks of age, various PCB Aroclor mixtures at either 2 or 20 ppm in their standard breeder diet. Data was taken at nine weeks, after establishment of steady state, for body fat and egg concentrations of the 6 different Aroclor mixtures. In order to calculate concentrations, Fries et al. (1977) assumed that the eggs weighed 50 grams and that the body fat was 10% of the full weight of body tissue. BCFs for these Aroclors were calculated in this assessment as the ratio of the egg fat concentration to the feed concentration, for egg BCFs, and the body fat concentration to the feed concentration. Fries, et al. (1977) had provided full egg concentrations, and these were converted to egg fat concentrations by assuming that lipid is 10% of the full egg weight. The assumption of Fries, et al. (1977) that the fat content of his tested tissues was 10% will be retained here. The BCFs for the Aroclors are shown in Table 4-8.

A noteworthy trend for this data, as observed by Fries, et al. (1977), is that the PCBs appear to be retained at greater amounts as the degree of chlorination continues but then drops off at the higher chlorinated congeners. This is apparent in Table 4-8, as the BCFs increase through Aroclor 1248, but then drop off for Aroclor 1254 for the low dose and at 1268 for the high dose. The BCFs for the eggs continue to increase suggesting that excretion through eggs continues to be a mechanism for removal through the high chlorinated congeners. It is unclear that the BCFs from this study are pertinent to the modeling of this assessment, not only because they are on Aroclors and not on the dioxin-like PCB congeners, but also because soil concentrations are unlikely to reach the 2-20 ppm level for individual dioxin-like PCBs. Still, it is the only data that could be found. Without rigorous justification, it will be assumed that the BCFs for the low dose of Aroclor 1254, 6.5 for egg fat and 7.4 for body fat, are appropriate for the dioxin-like PCB demonstrated in Chapter 5, 2,3,3',4,4',5,5'-PCB.

It should be noted that all bioconcentration or biotransfer parameters, such as the BCF, are qualified as second order defaults for purposes of general use. Section 6.2. of Chapter 6 discusses the use of parameter values selected for the demonstration scenarios, including a categorization of parameters. Second order defaults are defined there as parameters which are theoretical and not site specific, but whose values are uncertain in the published literature. The parameter values in this category should be considered carefully by users of the methodology.

● **Soil bioavailability B_s ; Feed, grass, and soil diet fractions, DF_f , DF_g , and DF_s ; and average feed, grass, and soil concentrations, AC_f , AC_g , AC_s :** The soil bioavailability is assumed to be 0.65, as it was for the beef/milk algorithm. It is important for users to understand that the BCFs were developed with this assumption. If other users believe it is more appropriate to assume that the BCFs as directly derived from the Stephens, et al. (1995) experiments are equally appropriate for soils, incidental vegetation, and feeds, than the BCFs need to be adjusted downward by multiplying them by 0.65. If doing this, users should then not apply a B_s in the calculation of chicken and egg concentrations for a free range or other scenario which has the chickens exposed to soil. Following on the lead of the Cal-EPA experiments, it will be assumed that soil is 10% of a free range chicken diet, and DF_s will be equal to 0.10. Since the chickens are free ranging, it also seems reasonable that they should be exposed to some incidental vegetation. No guidance could be found on the assignment of DF_g , but it does seem reasonable that the chicken would ingest less incidental vegetation than soil, particularly if their exposure to soil occurs when the chickens are feeding and their feed is spread out on a certain patch of ground worn bare to soil. On that basis, DF_g will be assigned a value of 0.05, and DF_f will be 0.85. The soil concentration, AC_s , could be modeled as in the case of erosion from a site of contamination to a site of exposure, or as in the case of stack emission deposition. For the latter case, the soil concentration assumed will be the untilled soil concentration. The soil concentration could also be specified, as in the case of soil contamination which is on-site. The incidental vegetation will be assumed to be leafy, as in grass, and the concentration in the grass will be modeled as grass would be modeled in the context of the source category. Based on the measurements of Chang, et al. (1989) and Stephens, et al. (1995), it will be assumed that the concentration on chicken feed will be zero.

4.3.5. Specific Cases of Soil Contamination

This section provides background information on specific sites of soil contamination which have been studied for the presence and impact of dioxin-like compounds. These include landfills used for disposal of ash from municipal waste combustion facilities, the disposal of sludge from pulp and paper mills, and sites of soil contamination typified by the sites monitored in the National Dioxin Study (in many cases, Superfund sites or sites that were in some stage of being considered for inclusion on the NPL list at the time of the study; EPA, 1987). Discussion of these particular sites does not imply that they represent the bulk of such sites nationally, or that they are discussed here based on any critical environmental or exposure rationale. They are discussed because they present unique issues for emissions and fate and transport of dioxin-like

compounds from sites of soil contamination, and because they have been studied. Issues discussed below are pertinent for other types of off-site soil contamination sites.

4.3.5.1. *Landfills Receiving Ash from Municipal Waste Incinerators*

Particular issues regarding landfills receiving ash include: the impact of soil cover on releases, the ash concentrations, the size of such landfills, the quantity of ash generated by incinerators, and the fugitive emissions that result from ash management. Key sources providing information for this section include a methodology document describing approaches to estimating environmental releases and exposures to ash (EPA, 1991), and a contractor report applying these types of methodologies using site-specific data from several ash landfills (MRI, 1990). Each of the identified topics will be discussed in turn.

- **Landfill Cover:** Whether or not ash is covered once it is disposed of at the landfill is critical in determining releases and subsequent exposures. Currently, practices at operating landfills vary from no coverage after disposal on active portions of the landfill to daily coverage of disposed ash. MRI (1990) visited six facilities disposing ash, including ash monofills and municipal solid waste landfills. In one of the facilities, an ash monofill located at the site of the combustor, the disposal area encompassed 15 acres and did not use daily cover until final elevation was reached. At that time, a clean cover of 2 feet of soil would be applied. At a second facility, located at the site of the combustor but landfilling municipal solid waste as well as ash, ash was used for different purposes, including a subbase roadbed material, as soil substitute for earth work, and as a daily cover for MSW receipts. An assumption of bare surfaces (i.e., no vegetation) during the period of landfilling activity, with concentrations of dioxin-like compounds equal to concentrations in the ash would appear to be appropriate assumptions for practices at these two landfills.

Where daily cover is employed, however, appropriate assumptions are not straightforward. Of the remaining four sites studied by MRI, two employed daily covers ("clean cover material" in one case and a "HDPE liner" in the other, sic), and daily coverage practices were not discussed for two sites. Approaches described for airborne emissions and erosion losses would have to be modified when daily cover is applied. First, losses of contaminants via overland soil or wind erosion could not be expected to occur when cover (soil cover or otherwise) is in place, although the active part of the landfill would be subject to erosion during an operating day. Even in that case, however, site-specific practices might include little or no ash disposal during periods of soil-erosion-producing storms. Depending on site-specific practices,

one might estimate annual erosion losses using methodologies described in this assessment, and then empirically reduce erosions losses based on these practices and scientific judgement.

Air emissions from active portions of the landfill, as in wind erosion and volatilization, also are obviously impacted by cover practices. These emissions would occur during the actual disposal. Wind erosion and volatilization fluxes could be estimated as given in earlier sections, and then reduced by two-thirds, which might correspond to an assumption of disposal during 1/3 of a day or a year, etc. When covered by soil or a synthetic cover, wind erosion losses would not occur. However, buried residues may diffuse through layers of clean soil and be released via volatilization.

Estimates of volatilization release via diffusion through clean cover have been made. A rigorous approach for such estimates is detailed in Hwang, et al. (1986). Use of this approach requires a computer to iteratively solve a partial differential equation, expressed in terms of a Fourier series. It can be shown, with these equations, that the vapor emission rate through such a cover will not reach steady state for hundreds of years. Hwang's approach was applied to an earlier assessment for 2,3,7,8-TCDD (EPA, 1988b). Calculations were performed for 2,3,7,8-TCDD contamination with a thickness of contamination of 8 ft, and clean caps ranging from 10 to 25 cm. The results of this exercise suggest that the average emission rate of a 70-year period are 1/4 to 1/5 of what they would be without the cap. Based on this exercise, a simple assumption might be made that a clean cap will reduce the average emission rate calculated without a clean cap by 80%. However, these results are not consistent with those described in Jury, et al. (1990). The analytical solution developed by Jury was demonstrated on 35 organic compounds. One exercise conducted by Jury was to estimate the cover thickness required to restrict volatilization to less than 0.7% of the mass incorporated in soil. For 2,3,7,8-TCDD, the thickness was estimated at 0.7 cm for a sandy soil and 0.2 cm for a clayey soil. This appears to contradict the work of Hwang since it shows an essentially insignificant loss for a cap much less thick than the 10-25 cm cap in the exercises using Hwang's approach. However, Jury's approach allows for assumptions on degradation of the buried compound. For that exercise, Jury assumed that the half-life for 2,3,7,8-TCDD was 1 year. This is a very rapid degradation rate, given information that the dioxin-like compounds resist degradation, particularly when not exposed to sunlight. On the other hand, the Hwang model assumes no degradation loss, and as such, the generalization from his exercise might be an overestimate. Hwang's exercise might also have overestimated since it assumed a rather thick 8-ft layer of subsoil contamination. From these arguments, it would appear that neither exercise appropriately evaluated the difference in volatilization in a no cover versus a cover situation.

The above discussions concerned flux calculations when cover practices are used. One set of adjustments discussed reduced a total potential flux of volatilized or wind eroded losses based on a portion of the time that the ash would be uncovered. A second discussion indicated that some loss via volatilization might be modeled with a clean cap. In any case, it is clear that cover practices will reduce losses. Cover practices must be considered when evaluating the exposure to ash disposed of in landfills.

● **Ash Concentrations:** A key consideration, of course, in modeling transport of dioxin-like compounds from an ash landfill is the concentration on the ash. Ash concentrations of dioxin-like compounds have been found to vary widely, from non-detect (generally less than 0.1 ppb) to the hundreds and thousands of part per billion. Table 4-9 appears in EPA (1991) and summarizes concentrations of dioxin-like compounds and PCBs found in fly, bottom, and combined ash. These data are a summary of 19 references, ranging in publication date from 1974 to 1990. It should be noted that, except for 2,3,7,8-TCDD and 2,3,7,8-TCDF, results listed are for congener groupings defined by degree chlorination.

● **Size of Landfill and Amount of Ash Landfilled:** The size of the landfill and the amount of ash applied daily or over time are both required for estimating exposures nearby. These can both be obtained from site-specific observations. Amounts of daily disposed ash are required to estimate fugitive particulate emissions, as will be discussed shortly. Amounts of daily or ultimate disposal are also tied to landfill size, or the portion of a landfill that is active on a daily basis. One common practice is to fill cells of a landfill one at a time, and once filled, to cover with a 2-ft (or so) layer of clean soil. The appropriate size in this case is the average size of a landfill cell. If daily coverage is applied, then the size for modeling purposes corresponds to the area over which daily coverage occurs. This can also vary depending on the depth of disposal during a day. A six-inch daily coverage, for example, would take twice as much space as a 1-ft depth of daily disposal. If the intent of a day's disposal is to cover over the entire area of an active cell, then depth of coverage need not be considered in determining landfill size.

Determination of landfill size (or the size of the active portion of the landfill) may be required in the absence of site-specific information, such as in the planning stages for a new incinerator. This is where details on landfill management need to be determined. One important detail, as already noted, is the amount of ash generated for daily disposal. Cook (1991) assumes that bottom and fly ash combined comprise about 11% of total receipts on a volume basis. However, a relationship between ash generated and solid waste received by an incinerator on a

mass basis is more useful for estimating daily disposal amounts. In an EPA (1990f) report on ash characterization, ash mass was estimated as an average of 29.5% of municipal solid waste received in five facilities studies, with a narrow range of 25-35%. This mass was estimated on a wet weight basis. Ash is wetted when exiting the incinerator, and water comprises 20-30% of the total weight at that point. If the ash is immediately trucked for landfill disposal, its total weight includes the weight of this quench water. Often ash is stored at the incinerator site in piles prior to disposal, that storage ranging from hours to days. In this circumstance, much of the quench water would have drained off or evaporated, and then the total weight hauled would be closer to a dry weight estimate. In summary, the amount of ash generated to be disposed of a daily basis can be estimated as: the daily receipt of municipal solid waste (tons) * a wet weight ash fraction (0.25-0.35) * a wet to dry weight conversion if appropriate (wet weight * 0.80, e.g.).

● **Fugitive Particulate Emissions:** Fugitive emissions can occur from the time ash exits the incinerator for temporary storage at the facility site (or immediate loading onto trucks for disposal) until ultimate disposal. Approaches to estimate fugitive releases from incinerator ash management are described in EPA (1991), and will be summarized here.

As noted, ash can be wet when exiting the quench tank. If stored at the facility site prior to disposal in a landfill, leaching from piles can occur. Because dioxin-like compounds are strongly hydrophobic, however, the impact of leaching is unlikely to occur much beyond the soil beneath and near the storage piles. If loaded onto trucks when very wet, leaking onto roadways may also occur. If these storage piles are left uncovered, they would of course be subject to erosion losses, which might move residues further from the piles than just leaching of water from the piles.

Of more concern than water-borne losses due to ash management are fugitive emissions of dry ash. Wind erosion, which can occur from open storage piles or uncovered portions of the landfill, is a fugitive emission that has been discussed for soil contamination. Specific practices in the management of ash can also result in fugitive emissions. Such practices include: 1) loading onto and dumping out of trucks, 2) truck transport from the incinerator facility to the landfill site, 3) truck or other traffic over paved or unpaved roadways at the incinerator site, at the landfill site, or other roadways containing contaminated dust, and 4) spreading and compacting of ash at the landfill site. A set of empirical emission factor equations for estimating fugitive particulate emissions, called "AP-42" equations, have been developed by EPA's Office of Air Quality Planning and Standards (EPA, 1985a; EPA, 1988a). Specifics on applying these equations for ash management are described in EPA (1991). An example of their application

using site-specific information for ash management is detailed in MRI (1990). An abbreviated listing of emission factor equations that have been used in these two publications are:

- Vehicular traffic over unpaved roadways. Dust on the surfaces of roads, both unpaved and paved, can become suspended due to vehicular traffic. When these roadways are near ash storage piles or within the landfill, that dust can become contaminated. The emission factor equation for emissions from unpaved roadways is:

$$E_{up} = 1.7 k_{unp} \left(\frac{scu}{12} \right) \left(\frac{Vs}{48} \right) \left(\frac{W}{2.7} \right)^{0.7} \left(\frac{nw}{4} \right)^{0.5} \left(\frac{365 - NP}{365} \right) \quad (4-48)$$

where:

E_{up}	=	emission flux for unpaved surfaces, kg/VKt (VKt equals vehicle kilometer traveled)
k_{unp}	=	particle size multiplier specific to the unpaved road emission flux equation, unitless
scu	=	silt content of unpaved roadway, %
Vs	=	vehicle speed, km/hr
W	=	vehicle weight, kg
nw	=	number of wheels per vehicle, unitless
NP	=	number of days with >0.25 mm precipitation per year, unitless

- Emissions off trucks in transit. Although no emission factor equations have specifically been developed for trucks while in transit from the incinerator facility to the landfill, such emissions can occur if the ash is dry, and partially or completely uncovered. The following equation for estimating emissions from open storage piles has been suggested for use in estimating fugitive emissions from trucks in transit (EPA, 1991; the emission factor equation from EPA, 1985a). Note that use of this equation will require specific management assumptions in order to estimate the number of uncovered hectares per day: the number of trucks in use per day, the surface area of trucks, the percent of uncovered area if a tarpaulin is used, the moisture content of ash, and so on.

$$E_t = 1.9 \left(\frac{sca}{1.5}\right) \left(\frac{f}{15}\right) \left(\frac{365 - NP}{365}\right) \quad (4-49)$$

where:

- E_t = particulates emitted from trucks in transit, kg/day/hectare
- sca = silt content material of ash, %
- NP = number of days with >0.25 mm precipitation per year
- f = percentage of time that the unobstructed wind speed exceeds 5.4 m/s.

● Loading and unloading. The unloading operations at the disposal site may result in the release of fugitive dust. The following emission factor equation provides emission factors for kilograms of particulate emitted per megagram (metric ton, or 1000 kg) of soil loaded and unloaded:

$$E_{lu} = 0.0016 k_{unl} \left(\frac{U_m}{2.2}\right)^{1.3} \left(\frac{MC}{2}\right)^{-1.4} \quad (4-50)$$

where:

- E_{lu} = emission factor for loading and unloading, kg dust/MT ash
- k_{unl} = particle size multiplier, unitless
- U_m = wind speed, m/s
- MC = material moisture content, %.

● Spreading and compacting of ash at the landfill. An emission factor specifically for ash spreading and compacting has not been developed. However, emission factor equations for similar applications have been applied for estimating fugitive emissions due to spreading and compacting. MRI (1990) used an AP-42 emission factor developed for dozer moving of overburden in western surface coal mines. Kellermeyer and Ziemer (1989) assumed that the spreading and compaction of ash was analogous to vehicular transport on unpaved surfaces, and used the emission factor for that process. A third possible assumption is that the processes of spreading and compacting are analogous to agricultural tillage. That emission factor equation for agricultural tillage is:

$$E_{at} = 5.38 k_{at} scs^{0.6} \quad (4-51)$$

where:

E_{at}	=	emission factor for agricultural tillage, kg/ha
k_{at}	=	particle size multiplier, unitless
scs	=	silt content of soil, %.

When applying such equations, there are further key issues to consider. These include:

- Concentrations on fugitive ash emissions: When such an emission occurs from ash surfaces, such as from storage piles, off trucks in transit, in spreading and compacting, and so on, than there is a good argument to assume that such concentrations on such emissions are "enriched" in comparison to an ash average. The argument here is similar to the argument for enrichment assumed for eroded soils: processes resulting in fugitive air emissions favor lighter particles with more surface area and hence more sites for binding. No data could be found to assign a value to an ash enrichment ratio. MRI (1990) did, however, take data on municipal waste combustor facility roadway dust, and based on that data and statistical evaluations, speculated that fly ash constituted the principal source of lead and cadmium found on paved surfaces. Since fly ash is finer than bottom or combined ash, one hypothesis for this finding is that fugitive emissions from ash management at the combustor site transported these finer particles to roadway surfaces. This is not to imply, however, that concentrations in dust suspended from roadways due to traffic should be higher in concentration than concentrations in ash - this enrichment concept only applies to ash surfaces themselves. Rather, the concentration on roadway suspended dust should be lower than on the ash. This is because contaminated dust on roadways mixes with clean dust from other sources. As noted, MRI (1990) did take roadway dust samples, and their data appears to place such a dilution factor (concentration on roadway dust divided by concentration on ash) in the range of 0.1 to 0.3. Specifically, they took particulate samples from landfill haul routes while at the same time taking samples of incinerator ash being delivered for disposal the same day. Each paired sample (roadway particulate and ash), were measured for four metals: As, Cd, Cr, and Pb. Several paired samples were taken on both paved and unpaved haul routes. Ratios were then generated for roadway particulate metal concentrations over ash metal concentrations. Results were: As - paved and unpaved ratios were similar and consistently near 0.1 (roadside particulate concentrations of As were 10% of ash

concentrations of As), Cd - paved and unpaved ratios were similar and ranged between 0.0 and 0.4, Cr - paved ratios ranged from 0.3 to 0.6, while unpaved had a wide range of 0.3 to 2.0, Pb - paved and unpaved ratios were similar between 0.0 and 0.2. For analogous situations - daily deliveries of contaminated ash - one might assume a dilution factor in the 0.1-0.2 range.

- Selection of values for emission factor equations: As noted, all these equations are empirical equations. They were developed from data on sites where such emissions occur, such as strip mining sites. EPA (1988a) describes the range of conditions over which such equations were developed. What is meant by "conditions" are such factors as the range of vehicle weights in the data set, the range in number of wheels on such vehicles, and so on. Application of these equations for situations not included within these ranges should be done cautiously. Very critical also is the selection of the particle size multiplier variable, k. These values range from about 0.10 to no higher than 1.0. Lower k values are used to estimate emissions of the smallest sized particles; generally particles less than 5 μm in diameter. Higher k values are used to estimate emissions of all sized particles less than a higher diameter, usually either 15 or 30 μm . If these equations are used to only estimate particulate inhalation exposures, than the k value corresponding to 10 μm sized particles, or inhalable sized particles, should be used. When used to estimate total emissions, than the highest k value listed should be used. Such estimations are appropriate when also evaluating impacts to off-site soils or vegetation.

- Controls for fugitive emissions: All these equations were developed when no fugitive emission controls were in place. Common controls for roadway dust suppression include wetting or use of a chemical dust suppressant. Ash transported in trucks is commonly wetted and/or a tarpaulin is used to control emissions off trucks. There is no guidance or data on the effectiveness of such controls, but they must be considered. In demonstrating these procedures, EPA (1991) assumed that controls on emissions resulted in 90% reductions in potential emissions. If a control is known to be in place and used on a regular basis, than this percent reduction is probably a reasonable starting assumption.

4.3.5.2. *Land Application of Sludge from Pulp and Paper Mills*

This discussion focuses on an assessment on the land application of sludge from bleached kraft and sulfite pulp and paper mills (EPA, 1990e). Focusing on this source of sludge does not imply that pulp and paper mills produce more sludge than other industries, or that sludge from pulp and paper mills contains more dioxin-like compounds than other sludges. However, it is known that dioxin-like compounds are found in pulp and paper mill sludges. Also, because of the 104-mill study in 1988, much information is available on the content and disposal of this

sludge (further information on the 104-mill study can be found in EPA (1990c,d)). Some of the issues briefly discussed below for pulp and paper mill sludges would also pertain to sludges containing dioxin-like compounds from other sources.

EPA (1990e) described frequency distributions of concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF for 79 mills reporting this information and also broke out the data based on disposal option. Although EPA (1990e) used the disposal option breakout of concentrations in their assessment of the impacts of the various options, it is not felt that the disposal option of choice is based on concentration. Over all options, the median (50% percentile as given in EPA (1990e)) and maximum 2,3,7,8-TCDD concentrations found in sludges were 51 and 3800 ng/kg (ppt), respectively. The median and maximum 2,3,7,8-TCDF concentrations found were 158 and 17100 ppt.

Fate and transport for contaminants in sludge is dependent on disposal means. Of the approximate 2.5 million metric tons of pulp and paper mill sludge generated annually (as estimated in the 1988 104-mill study), five principal options for disposal were noted: landfilling (44% of all sludge disposed), surface impoundments (24%), land application (12%), incineration (12%), and distribution and marketing (8%). Impacts by incineration were not discussed in EPA (1990e) and are not discussed in this section. Key issues pertaining to each disposal issue are now discussed.

- **Landfilling:** The issue of coverage as discussed above for ash landfills is relevant for any landfill. However, fugitive particulate emissions during sludge handling and disposal is not an issue as it was for disposal of ash from incinerators due to the differences in moisture content. Sludge is much higher in moisture at the time it is disposed of in comparison to ash - with moisture contents as high as 90%.

- **Surface Impoundments:** It was assumed in EPA (1990e) that sludge disposed of in surface impoundments have a higher moisture content as compared to sludge disposed of in landfills. Surface impoundments were located at the mill site, explaining the assumption for a higher moisture content. A surface impoundment in the EPA (1990e) assessment was defined as a facility in which the sludges are stored or disposed on land without a cover layer of soil. For this type of management, soil cover would not be an issue. Concentrations would be those measured in the sludge. Also, vegetative cover would be expected to be minimal, which would influence parameters associated with soil erosion.

● **Land Application:** Twelve percent of all sludge produced annually was land applied. Four of the 104 mills applied the sludge to forest land, two mills land applied the sludge to agricultural land, and two mills used the sludge for abandoned mine reclamation. The high organic matter content (EPA (1990e) assumed a 25% organic carbon fraction in sludge) and high fraction of clay-sized particles make sludge an attractive soil amender. Sludge is either applied to the land surface with or without incorporation. When not incorporated, sludge can be assumed to replace surface soils and concentrations would be those in the sludge. When incorporated, soil concentrations can be estimated simply as (in mg/kg): (mass of contaminant added, mg)/(mass of sludge added, kg + mass of soil in mixing zone, kg). One key issue when incorporated is the number of years of such treatments. Most of the land application uses of paper and pulp mill sludges reported in EPA (1990e) made applications in only one year. As easily seen in the above suggested equation, higher concentrations result with more years of incorporation. The other key issue with incorporation, of course, is the depth of incorporation. For agricultural applications, the depth of incorporation assumed in EPA (1990e) was 15 cm, similar to the 20 cm incorporation assumed for home vegetable gardening in this assessment. For silvicultural uses, the assumption in EPA (1990e) was 2.5 cm, which corresponds to some but minimal mixing. For abandoned mine reclamation, the assumption was 0 cm incorporation. Routes of exposure might also vary from focuses in this document depending on land application choice. When applied to agricultural land, impacts to food crops would demand particular attention (the procedures in this assessment were demonstrated with home grown vegetables, although of course impacts to food crops are critical when agricultural field soils are impacted by dioxin-like compounds). When applied to forest land, ecological impacts might warrant particular attention, as was discussed and demonstrated in EPA (1990e). A final issue to consider when land applying sludge to land is a rate of dissipation/degradation of dioxin-like compounds. Landfills and surface impoundments have ongoing surface applications and over time, the total depth of applications in the range of meters, so an assumption of a constant source strength over a period of exposure, as was assumed in this assessment for soil contamination sources, is reasonable. However, if only a few centimeters of surface soil are impacted, which might be the case for single applications to land and/or surface applications with no incorporation, an assumption of dissipation may be warranted. EPA (1990e) assumed no degradation of 2,3,7,8-TCDD in their assessment of impacts from land applications.

● **Distribution and Marketing Uses:** The volume of sludge distributed and marketed was approximately 8% of the total amount of sludge generated for the 104-mill study. For this

use, sludge was composted and then sold as a soil amendment in residential, agricultural, and commercial settings. More attention to the dermal contact pathway appears appropriate for this usage. Site-specific factors, and the values for these factors used in EPA (1990e), include: 1) depth of incorporation - 0, 15 and 25 cm in assumptions characterized as high, best, and low estimates, 2) garden size - 0.016 and 0.022 hectares characterized as low/best estimate and high, and referencing a national gardening survey, 3) rate of application - between 5 and 20 dry metric tons per hectare references a USDA publication on use of sewage sludge compost for soil improvement and plant growth, and 4) years of using such compost - 20 without specific reference. The years of application is needed for estimating soil concentrations during and after the period of exposure, using a simple ratio as discussed above in land application.

4.3.5.3. Sites Studied in the National Dioxin Study

The National Dioxin Study (EPA, 1987) focused on sites of known or suspected contamination of soil by 2,3,7,8-TCDD. There were 7 "Tiers" of investigation, with roughly decreasing expectations of finding 2,3,7,8-TCDD. Tiers 1 and 2 included 2,4,5-TCP production and associated disposal sites (Tier 1) and sites where 2,4,5-TCP was used as a precursor in the manufacture of pesticidal products and associated disposal sites (Tier 2). These tiers had the highest expectation for finding 2,3,7,8-TCDD. There were originally thought to be 450 sites that would fall in Tiers 1 and 2, but after investigation, only 100 sites were included for study. Some were downgraded into Tier 3. Of the 100 sites studied, 20 were on or were proposed for inclusion in the Superfund National Priorities List. Tiers 3 and 5 were associated with 2,4,5-TCP formulation (Tier 3) and use (Tier 5). Tier 6 were organic chemical or pesticide manufacturing facilities where 2,3,7,8-TCDD was suspected of being present. Tier 4 included combustion sources and are not discussed further in this section. Tier 7, basically an examination of background areas, are also not discussed here.

Issues that are identified as important in fate and transport modeling for this subcategory of off-site sources include concentrations, the possibility of ground water contamination, and site-specific characterization. These are discussed in turn.

- **Concentrations:** Only 11 of the 100 Tier 1 and Tier 2 sites were eventually classified as requiring "no further action" because 2,3,7,8-TCDD soil concentrations were very low, < 1 ppb, or not detected (with detection limits generally at 1.00 ppb). Where it was detected, a general trend was to find very high concentrations where 2,4,5-TCP production wastes were stored or disposed of, with much lower concentrations at soils near these particular

areas. At hot spots, concentrations were as high as 2,000 parts per million, but generally soil concentrations were in the parts per billion. It was this parts per billion generalization that led to the assignment of a 1 ppb soil concentration for the demonstration of the off-site source category in Chapter 5. There were findings in the low ppb range for Tiers 3, 5, and 6, but at much lower frequency and no findings higher than the tens of ppb range. For exposure assessments, the characterization of soil concentrations in a site containing hot spots has to be carefully considered. For site evaluations and proposed options for remediation, an areally weighted average might be considered, although this could dilute loss estimates depending on the area chosen - choosing a large area corresponding to property lines might, for example, lead to an "average" concentration orders of magnitude lower than concentrations found in hot spots. One approach which should be considered is a "hot spot" impact compared to an areally averaged impact. It should also be remembered that removal of highly contaminated soils is a common practice and another option for evaluation would be a concentration assuming hot spots are removed.

● **Potential for Ground Water Contamination:** PCBs have been found in ground water in sites associated with dielectric fluids of transformers. Oils can migrate through soils as a separate immiscible phase and reach ground water, which has been the common explanation for PCB impacts to ground water. Ground water contamination by 2,3,7,8-TCDD has very rarely been found in ground water, although it has been released to the environment in an oil matrix. The Times Beach area of Missouri is the principal example of this release, where waste oils containing 2,3,7,8-TCDD were used for dust control. Ground water sampling did occur in many of the Tier 1 and 2 National Dioxin Study sites, but the results were mostly non-detects. One occurrence at 0.18 ppt was noted for the Hyde Park site of Hooker Chemical in Niagara, NY, and a high of 1.8 ppb was found in an on-site monitoring well at National Industrial Environmental Services in Furley, KS. There were, however, numerous high occurrences in sub-soil samples in hot spot areas, in bottom sediments of evaporation lagoons, and so on, in the hundreds of ppb range.

There have been some limited experimentation showing different patterns of 2,3,7,8-TCDD migration in soils in the presence of solvents or in an oily matrix. Palusky, et al. (1986) studied the mobility of 2,3,7,8-TCDD in soils associated with each of 6 solvents. Migration was found to be higher with aromatic solvents and chloroform in comparison to saturated hydrocarbons and methanol. They speculated that the extent of migration related to the solubility of 2,3,7,8-TCDD in the solvent. Puri, et al. (1989) studied the migration potential of 2,3,7,8-

TCDD in soil, water, and waste oil mixtures. Over time, they observed a reversible sorption pattern of TCDD, and concluded that a carrier medium with a significant amount of waste oil would play a dominant role in the movement of TCDD through soils.

● **Site-specific Characterization:** In the case of landfills or sludge land application sites, the assignment of a soil concentration and an area can be made with some reasonableness. Such is not the case with the industrial contamination sites such as those studied in the National Dioxin Study, as briefly discussed above in the concentration bullet. Most of the sites studied in the National Dioxin Study were in the order of tens of hectares to below ten hectares. On the other hand, the Dow Chemical site in Midland, Michigan is described as a site 607 ha in size (Nestrick, et al, 1986). That area corresponds to the size of the property, and the many soil sampling sites within that area were described as "background". Several of the pesticide formulator sites studied in Tier 3 were 2 hectares or less in size. Many of the them were extensively or partially paved with buildings, which complicate fate and transport modeling. Some of the Tier 5 sites of 2,4,5-TCP use were agricultural fields, which are less complicated to describe. However, two sites were described as 2500 acres in size, which again is very large and makes assignment of an average soil concentration non-trivial. Other use sites were described as railyards and railroad rights of way. While estimates of loss into air could be made in complicated sites such as these, use of soil erosion modeling becomes very complicated if not undoable with paved areas, buildings, drainage ditches, roads, and the like.

4.4. ALGORITHMS FOR THE STACK EMISSION SOURCE CATEGORY

Contaminants emitted from incinerator stacks are transported in air and deposit on the exposure site, water bodies that may be used for drinking or fishing purposes, and on surrounding land. Chapter 3 describes the application of the ISCST3 model to obtain vapor-phase air concentrations and deposition rates of particles at a specified distance from an example stack emission source. These quantities are assumed to be given for purposes of discussion in this section; further discussion of the air transport modeling is given in Chapter 3.

Estimating soil concentrations based on particulate depositions follows a similar approach as estimating exposure site soil concentrations resulting from erosion of contaminated soil from off-site areas of contamination. Section 4.4.1. describes how soil concentrations are estimated given total (wet plus dry) deposition rates. Surface water impacts are assumed to result from direct deposition onto surface water bodies as well as erosion from the impacted effective drainage area. This solution is an extension of the solution given in Section 4.3.1. for the soil

contamination source category, and is given in Section 4.5.2. Following now are bullet summaries for similarities and small refinements to algorithms previously discussed:

- **Air impacts:** The atmospheric transport modeling described in Chapter 3 was comprised of two computer simulations: one which considered that emissions were in a vapor form and were transported as such, and one which considered that emissions were in particle form and likewise were transported as such. The result of the vapor-phase runs was a unitized ambient air concentration at various distances up to 50 km in all directions from the stack. Only the results in the predominant wind direction were used in this demonstration. The result of the particle-phase runs were an ambient reservoir of air-borne contaminants sorbed to particulates (used only for inhalation exposures), and wet and dry deposition unit rates also at various distances up to 50 km. By "unitized", what is meant is that emissions for the vapor or particle runs can be thought of as "1" mass/time (g/sec) emissions. Results for all distances are linear with respect to this emission rate; that is, if the rate of vapor contaminant determined to be emitted is "5", than ambient air concentrations at any location are 5 times what they are when "1" is assumed to be emitted. The same holds true for emissions in the particle phase. Chapter 3 developed a framework for assigning a vapor and a particle fraction for specific dioxin congeners. For example, 2,3,7,8-TCDD was assumed to have a vapor fraction of 0.51 (51% was in vapor form) and a particle fraction of 0.49. The final model results for air concentrations, and dry and wet deposition rates for all congeners, starting from these unit model runs and then incorporating congener-specific emission rates and vapor/particle splits, are given in Tables 3-12 to 3-17. The vapor-phase air concentrations were used to model vapor phase transfers in the vegetative bioconcentration algorithms. They were also used, summed with the simulated reservoir of particle-bound contaminants, to estimate the total reservoir of contaminant available for inhalation exposures.
- **Vegetative impacts:** The rates of wet and dry deposition modeled by ISCST3 were used to determine vegetative impacts. The model for particle deposition impacts to vegetation is described in Section 4.3.4.2 above. Of course, this above section solves for dry deposition as a reservoir times a dry deposition velocity (for dry deposition), and as a reservoir times rainfall and a washout factor (for wet deposition); such a solution is not required for the stack emission source category

since the deposition totals are estimated by the ISCST3 model. Other parameters for the vegetative model - the B_{vpa} (air-to-leaf vapor transfer factor), the R_w (fraction of wet deposition retained on vegetation surfaces), crop yields and interceptions, and the vegetative washout factor, k_w , are used for the stack emission source category.

- **Biota concentrations:** The algorithm estimating concentration in fish tissue based on bottom sediment concentrations is the same as in previous source categories. Modeled rates of contaminant deposition on particles onto the exposure site are used to estimate a "tilled" and an "untilled" soil concentration, as described below in Section 4.4.1. Underground vegetable concentrations are a function of tilled soil concentrations. The soil concentration used for cattle soil ingestion is untilled. Beef and milk concentrations are again a function of vegetative and soil concentrations, diet fractions, and bioconcentration and bioavailability factors as described in Section 4.3.4.3.

4.4.1. Steady-State Soil Concentrations

Chapter 3 describes the use of the ISCST3 Model to estimate the particulate phase deposition rates at the exposure site. This total deposition rate, F , includes both dry and wet deposition, and is used to estimate the soil concentrations. The deposition of contaminated particulates from the air is assumed to be somewhat analogous to the process of eroding contaminated soil from an off-site source depositing on an exposure site. Specifically, the following assumptions are also made: 1) only a thin layer of soil becomes contaminated, 2) this layer is either "untilled" or "tilled", depending on surface activities, and 3) surface residues are assumed to dissipate with a half-life of 25 years corresponding to a first order decay rate of 0.0277 yr^{-1} . Considerations of upgradient erosion and exposure site soil removal are not made. Depositions occur over the exposure site and surrounding land area on an on-going basis. It might be said that upgradient soil concentrations are similar to exposure site concentrations at all times. Like the soil source categories, a tilled mixing depth of 20 cm, and an untilled mixing depth of 2 cm is assumed for this source category. The qualitative mass balance statement (similar to the one made above in Section 4.3.2, with ΔC equaling change in exposure site soil concentrations over time) can now be made as:

(the incremental addition to C resulting from the change in deposition of stack emitted particulates) -

ΔC = (the incremental subtraction of C resulting from degradation of residues at the exposure site)

This is mathematically stated as:

$$\frac{dC}{dt} = \frac{F}{M} - kC \quad (4-52)$$

where:

C = the exposure site soil concentration, mg/kg
 F = deposition rate of contaminant on particles, mg/yr
 M = mass of soil at exposure site into which contaminant mixes, kg
 k = first order dissipation rate constant, 1/yr.

The solution to this equation is:

$$C = \frac{F}{kM} (1 - e^{-kt}) \quad (4-53)$$

which computes C as function of time, t. Similar to the assumption made above in Section 4.3.2, the steady state solution for C is simply F/kM. The deposition rates supplied by the ISCST3 model are in units of g/m²-yr, so a conversion to mg/yr requires a multiplication by the land area of the exposure site and a multiplication of 1000 mg/g. Procedures to estimate M are given above in Section 4.3.2.

4.4.2 Surface Water Impacts

The solution for stack emission impacts to surface water bodies is an extension of the solution for the soil contamination source category described in Section 4.3.1. Stack emissions deposit onto soils within the effective drainage area to result in an average basin-wide soil concentration. Soil erosion then delivers contaminants to surface waters as in Section 4.3.1. Stack emissions also directly deposit onto and impact the surface water body as well. All the assumptions laid out at the beginning of Section 4.3.1 apply here as well. New quantities needed for this solution include: a rate of contaminant deposition onto soils of the effective drainage area used to estimate average soil concentrations (such concentrations are estimated using the

approach given in Section 4.4.1. above), a rate of contaminant deposition onto the water body, and a rate of particulate matter deposition onto the water body.

Equations (4-1) through (4-8) are now displayed again with these additions.

$$C_{swb} ER_w + DEP_c = C_{wat} V_{wat} + C_{ssed} M_{ssed} + C_{sed} M_{sed} \quad (4-54)$$

where:

C_{swb}	=	concentration on soil entering water body, mg/kg
ER_w	=	total watershed annual soil erosion, kg/yr
DEP_c	=	total annual direct deposition of contaminant, mg/yr
C_{wat}	=	dissolved-phase concentration in water column, mg/L
V_{wat}	=	water body annual volume, L/yr
C_{ssed}	=	concentration on suspended sediment, mg/kg
M_{ssed}	=	mass of suspended sediment introduced per year, kg/yr
C_{sed}	=	concentration on sediment settling to bottom, mg/kg
M_{sed}	=	mass of bottom sediment introduced per year, kg/yr

Mass balance and equilibrium equations continue:

$$ER_w + DEP_p = M_{ssed} + M_{sed} \quad (4-55)$$

$$M_{ssed} = f_s ER_w + f_{sd} DEP_p \quad (4-56)$$

$$M_{sed} = (1 - f_s) ER_w + (1 - f_{sd}) DEP_p \quad (4-57)$$

$$C_{wat} = \frac{C_{ssed}}{KD_{ssed}} \quad (4-58)$$

$$C_{sed} = C_{ssed} \frac{OC_{sed}}{OC_{ssed}} \quad (4-59)$$

where:

- DEP_p = total annual direct deposition of particulate matter, kg/yr
- f_s = fraction of annual erosion remaining as suspended materials, unitless
- f_{sd} = fraction of annual deposition remaining as suspended material, unitless
- Kd_{ssed} = soil-water partition coefficient for contaminant in suspended sediment, L/kg
- OC_{ssed} = fraction organic carbon in suspended sediment, unitless
- OC_{sed} = fraction organic carbon in bottom sediment, unitless

Substituting again as in Equation (4-7):

$$C_{swb} ER_w + DEP_c = C_{ssed} \left[\frac{V_{wat}}{Kd_{ssed}} + f_s ER_w + f_{sd} DEP_p + \frac{OC_{sed}}{OC_{ssed}} \right] \left[(1 - f_s) ER_w + (1 - f_{sd}) DEP_p \right] \quad (4-60)$$

As before, the bracketed quantity in the right hand side of Equation (4-60) can be termed ϕ , so that C_{ssed} can be solved as $(C_{swb} ER_w + DEP_c)/\phi$. The numerator in this term can be expanded to describe contaminant contributions by the effective drainage area which has received depositions, the first quantity in the numerator, and to describe direct depositions, the second quantity:

$$C_{swb} ER_w + DEP_c = C_w SL_w A_w E SD_w + RDEP_c A_{wat} 1000 \quad (4-61)$$

where:

- C_{swb} = concentration on soil entering water body, mg/kg
- ER_w = total watershed erosion, kg/yr
- DEP_c = annual deposition of contaminant on water body, mg/yr

E	=	enrichment ratio, unitless
C_w	=	average soil concentration of dioxin-like compound in effective area of watershed, mg/kg
SL_w	=	average unit soil loss for land area within watershed, kg/ha-yr
A_w	=	effective drainage area of watershed, ha
SD_w	=	sediment delivery ratio for watershed, unitless
$RDEP_c$	=	rate of contaminant deposition, g/m ² -yr
A_{wat}	=	area of water body, m ²
1000	=	converts g to mg

Again as before, the right hand side of Equation (4-61) can be termed, ρ , and the concentration in suspended sediment, C_{ssed} , is equal to ρ/ϕ . Other water body concentration terms, C_{wat} and C_{sed} , can now be solved using Equations (4-58) and (4-59). Guidance on these terms and assignment of values for the demonstration scenarios in Chapter 5 is now given.

- **C_{swb} and ER_w :** Equation (4-61) shows all the terms necessary to arrive at an estimate of the annual contaminant entry into the water body via erosion, the $C_{swb} * ER_w$ term. Section 4.4.1 describes the algorithm to estimate soil concentrations given a deposition rate of contaminant. One deposition rate will be chosen to represent average deposition rates over the effective drainage area of the watershed (the effective drainage area is termed A_w). This rate will be the rate given in ISCST3 modeling at 5.0 kilometers. Tables 3-15 and 3-16 (Chapter 3) display wet and dry deposition rates for this distance. These rates are added to arrive at total deposition, shown in Table 3-17. Second, a representative mixing depth to characterize average watershed soil concentrations needs to be selected. Previous algorithms used a mixing depth of 20 cm for tillage activities, specifically home gardening, and 2 cm for non-tilled soil concentrations. For the sake of demonstration, it will be assumed that a representative watershed depth will equal 10 cm, which might be interpreted as an average of tilled and untilled lands within the effective drainage area. The values for SL_w (6455 kg/ha-yr), A_w (100,000 ha), ER (3), and SD_w (0.06) were all given and discussed in Section 4.3.1. and will not be repeated here.

- **DEP_c:** The second quantity of Equation (4-61) describes the annual input to the surface water body that comes from direct deposition. This term is $RDEP_c * A_{wat} * 1000$, where $RDEP_c$ is the rate of contaminant deposition onto the water body (g/m²-yr), A_{wat} is the area of the water body (m²), and 1000 converts g to mg. The rate of contaminant deposition at 5 km will

also be used to describe direct deposition impact to the surface water body. Depositions nearer to the emission source will be greater and depositions further from the emission source will be less. The area of the water body has not been required for any other reason, and one will now be given. First, the effective drainage area of 100,000 ha is reasonably large and has resulted in a river with an annual flow volume of 4.8×10^{11} L/yr (4.8×10^8 m³/yr). This volume is also equal to the average cross sectional area of the river (m²) times stream velocity (m/yr). Assuming a stream velocity of 4.73×10^6 m/yr (15 cm/sec; ½ ft/sec), which is reasonable for a river, the cross sectional area is solved as 100 m². An average 5 m depth and 20 m width appear reasonable. This width times the stream length would give stream surface area, A_{wat} . Assuming a rectangular shaped watershed, dimensions of 500 ha wide by 2,000 ha long (to arrive at the 100,000 ha effective drainage) seem reasonable. This length of 2,000 ha translates to 200,000 meters, and the full surface area of the stream is 4×10^6 m². This will be the value assumed for A_{wat} .

- **DEP_p:** The rate of particulate deposition onto the lake is required to achieve a mass balance of all annual soil erosion + particle deposition contributions to water body solids. The rate of particulate matter emitting from the stack and arriving at downwind locations was not supplied in Chapter 3. Goeden and Smith (1989) modeled the impacts of a resource recovery facility to a local water body. In their analysis, they assumed that the stack emitted 4.63 g/s particulate matter and that the annual deposition of stack-emitted particulate matter to the nearby impacted water body was 0.03 g/m²-yr. This deposition rate will be adopted for this assessment. Now, with the surface area as solved for above at 2×10^6 m², the total particle deposition, DEP_p is 60 kg/yr.

- **f_s and f_{sd}:** These are the fractions of total erosion and depositing particles remaining as suspended materials within a year. As discussed in the solution for the contaminated soil source category in Section 4.3.1, f_s was solved for as: a value for total suspended solid, TSS of 10 mg/L, multiplied by a total flow volume V_{wat} of 4.8×10^{11} L/yr, divided by the total erosion into the water body, 1.29×10^7 kg/yr. This resulted in an f_s of 0.36. Note that this implies a total suspended load of 480,000 kg/yr. It could be assumed that the minuscule 60 kg/yr of particles directly depositing onto the stream remain in suspension during the year, on the basis of being smaller in size than eroded soil. This assumption will, in fact, be made, but it will be supported as follows.

In a quiescent water body, settling occurs through gravity and can be expressed in terms of Stokes Law:

$$V_s = (g / 18\mu) (\rho_s - \rho) d^2 \quad (4-62)$$

where:

V_s	=	Stokes settling velocity, cm/sec
g	=	acceleration of gravity, 980 cm/sec ²
μ	=	absolute viscosity of water, g/cm-sec (poise)
	=	0.089 g/cm-sec @ 25 C
ρ_s	=	particle density, g/cm ³
ρ	=	density of water, 1 g/cm ³
d	=	particle diameter, cm

For purposes of this discussion, a reasonable assignment of particle density of is 2.5 g/cm³ for depositing particles or eroding soil. Therefore, making substitutions, the right hand side of Equation (4-62) reduces to 918 d².

Now, assumptions for the particle sizes of eroding soil and depositing particles can be made to arrive at a ratio of settling velocities, V_{soil}/V_{spart} . The basis for assigning an enrichment ratio for delivery of contaminants via soil erosion was that fine-sized particles were the ones eventually reaching the water body via erosion. Lick (1982) states that a major fraction of the sediments (suspended and bottom) in the Great Lakes are fine grained, silts and clays, and that data from Lake Erie indicates that 90% of the sediments are of this category. Brady (1984) shows USDA's classification of soils according to particle size, and gives a range of 0.0002 to 0.005 cm for silt sized particles and less than 0.0002 for clay size particles. The following assumptions are made to arrive at a representative diameter for particles in eroded soil: eroded soil is comprised of a 50/50 split of these two sized particles, silt-sized particles are, on the average 0.0026 cm in diameter, and clay size particles are 0.0001 cm in diameter. With these assumptions, the average particle size for eroding soil is 0.0014 cm. The settling velocity for a 0.0014 cm particle is 1.8×10^{-3} cm/sec. In Section 3.4.3, Chapter 3, the argument was developed that 87.5% of the total emission rate of dioxin-like congeners would be associated with particles less than 2 μ m. The basis of this argument was a surface area to volume ratio, with smaller particle sizes having significantly larger ratios. This does not mean that 87.5% of the 1 kg/yr depositing particles are of this size. However, for this discussion, the size of depositing particles will be assumed to be 2 μ m (2×10^{-4} cm), since these size particles deliver most of the dioxin-like compounds to the water body (and the ultimate purpose of this exercise is to determine a

value for the fraction of depositing particles which remain suspended and impact suspended sediment concentrations). The settling velocity, V_{spart} , is estimated as 3.7×10^{-5} cm/sec.

The ratio $V_{\text{soil}}/V_{\text{spart}}$ is about 50. Said another way and with all the assumptions and simplifications made above, depositing particles will remain in suspension 50 times longer than eroding soil in a quiescent water body.

Given this high a difference in settling velocities, it seems reasonable to assume f_{sb} equals 1.0. The fraction of soil erosion remaining in suspension, f_s , will be estimated given TSS, V_{wat} , etc., as before (see Section 4.3.1), only DEP_p (the total amount of depositing particles, in kg/yr) will comprise a given increment of suspended materials when solving for f_s .

- V_{wat} , OC_{ssed} , OC_{sed} , and Kd_{ssed} : These have all been discussed in Section 4.3.1. The values for these parameters in the demonstration scenarios in Chapter 5 are: $V_{\text{wat}} = 4.8 \times 10^{11}$ L/yr, $\text{OC}_{\text{ssed}} = 0.05$, $\text{OC}_{\text{sed}} = 0.03$, and $\text{Kd}_{\text{ssed}} = \text{OC}_{\text{sed}} * \text{Koc}$, where Koc is the organic partition coefficient of the contaminant.

4.5. ALGORITHMS FOR THE EFFLUENT DISCHARGE SOURCE CATEGORY

Dioxin-like compounds can be released to waterways via various types of effluent discharges such as discharges from municipal waste water treatment facilities and pulp and paper mills using chlorine bleaching. These emissions have declined substantially in recent years, especially from pulp and paper mills. Since the procedures for considering point source discharges to waterways are somewhat different than those associated with the nonpoint source procedures for soil contamination and stack emissions, they are covered separately in this section. This source category is also different from others in that effluent discharges into surface water bodies are assumed only to impact fish and water.

The approach used in this report is an extension of the "simple dilution" model described in the Superfund Exposure Assessment Manual (EPA, 1988c). Other models are available which offer more spatial and temporal resolution than the model described here. One such model is the EXposure Analysis Modeling System, or EXAMS (Burns, et al., 1982, and Burns and Cline, 1985). The EXAMS and a simple dilution model were both applied in an assessment of effluent discharges from pulp and paper mills (EPA, 1990d). In this assessment, 98 of the 104 pulp and paper mills were modeled with both models using site-specific information (water body flow rates from STORET for all but 6 of the mills, effluent flow rates and contaminant discharges, etc.). Three key quantities - one model result and two model parameters - led to a range of exposure conditions for humans consuming fish impacted by discharges from these pulp and

paper mills: a water column concentration, a bioconcentration factor (BCF) applied to the water column concentration to get fish tissue concentration, and a fish ingestion rate. The simple dilution model was used to estimate total water concentrations - i.e., mg TCDD total/L water. The EXAMS model was used to estimate dissolved phase water column concentration - i.e., mg TCDD dissolved in water column/L water. Then, with each set of water concentrations, two sets of exposure estimates (a low and a high estimate, in one sense) were generated - one with a BCF of 5,000 and a fish ingestion rate of 6.5 g/day, and one with a BCF of 50,000 and a fish ingestion rate of 30 g/day. Note that in deriving the range of results in that exercise, the BCF was applied to both a total and a dissolved phase water concentrations. EPA (1993b) and EPA (1995) discuss several bioconcentration/bioaccumulation empirical parameters for 2,3,7,8-TCDD, and makes the clear distinction for those which are to be applied to a total water concentration versus those applied to a concentration in the dissolved phase. The dilution and EXAMS model study indicated that the simple dilution model generally estimated higher water column contaminant concentrations compared to the EXAMS model, although this trend was not consistent among all water bodies modeled. The results from both models were comparable when the receiving water body had relatively low suspended solids concentration.

One key limitation of the EXAMS and the simple dilution model for use with dioxin-like compounds in aquatic systems is that they do not account for sediment transport processes. The EXAMS model was designed to determine the fate of transport of contaminants in the dissolved phase. Another spatially and temporally resolved model for this source category is the Water Analysis Simulation Package, the most up-to-date version termed WASP4 (Ambrose, et al., 1988). This model does include sediment processes and has been applied in a comprehensive evaluation of 2,3,7,8-TCDD bioaccumulation in Lake Ontario (EPA, 1990b). It requires extensive site-specific parameterization, but should be considered for more detailed site-specific evaluations of strongly hydrophobic and bioaccumulating contaminants such as the dioxin-like compounds.

The dilution model described below will be demonstrated in Chapter 5 with a set of data developed using site-specific data from the 104 pulp and paper mills of the 104-mill study. As will be discussed below, a hypothetical effluent discharge will have characteristics developed as the average of key characteristics from the 104 mill study. These key data include: flow rates of the receiving water bodies, suspended solids concentration in these receiving water bodies, effluent discharge flow rates, suspended solids in the effluent discharges, organic carbon content of solids in the effluent stream, and discharges of 2,3,7,8-TCDD.

4.5.1. The Simple Dilution Model

The principal assumption for the simple dilution model is that contaminants released into a water body uniformly mix and equilibrate with the surrounding water in an area near the effluent discharge point. This area is commonly referred to as a "mixing zone". For application of this model with dioxin-like compounds, what is desired is a concentration on the suspended solids in this mixing zone. Multiplication of the organic carbon normalized concentration on suspended solids and a Biota Suspended Solids Accumulation Factor, or BSSAF, will result in a concentration of contaminant in fish lipids. This is defined similarly to the BSAF used for other source categories of this assessment, except that the organic carbon normalized concentration is that of suspended solids rather than of bottom sediments.

The BSSAF is one of several empirical factors discussed for estimating the impact to fish in water bodies impacted by 2,3,7,8-TCDD (EPA, 1993b). Others include the BSAF, total and dissolved phase bioconcentration factors (BCFs), and total and dissolved phase bioaccumulation factors (BAFs). BAFs and similar to BSAFs and BSSAFs in that all three reflect total exposure of fish to contaminant, including water column, sediment, and food chain exposures. The BCFs reflect water column exposures only. EPA (1993b) states that there is currently no data available on organic carbon normalized concentrations of dioxin-like compounds on suspended solids, hence no basis to compare BSAF and BSSAF. This assessment assumes a similar numerical assignment of BSSAFs and BSAFs.

The total water concentration in a simple dilution model is:

$$C_{tot} = \frac{MASS_c}{Q_e + Q_u} \quad (4-63)$$

where:

- C_{tot} = total water concentration, mg/L
- $MASS_c$ = mass of contaminant in discharge, mg/hr
- Q_u = harmonic mean flow at a point just upstream of effluent discharge, L/hr
- Q_e = effluent flow, L/hr

Dissolved phase and suspended sediment concentrations are then estimated using an approach developed by Mills, et al. (1985) and others:

$$C_{wat} = \frac{C_{tot}}{1 + (Kd_{mix} TSS_{mix} 10^{-6})} \quad (4-64)$$

$$C_{ssed} = Kd_{mix} C_{wat} \quad (4-65)$$

where:

C_{wat}	=	dissolved-phase water concentration of contaminant, mg/L
C_{tot}	=	total water column concentration, sorbed + dissolved, mg/kg (note: mg/kg is essentially equal to mg/L since 1 L \approx 1 kg)
Kd_{mix}	=	suspended sediment-water partition coefficient for contaminant in mixing zone, L/kg
TSS_{mix}	=	total suspended solids in water column in mixing zone, mg/L
C_{ssed}	=	concentration of dioxin-like compounds on suspended sediments, mg/kg
10^{-6}	=	converts mg/L to kg/L

The total suspended solids concentration in the mixing zone is a function of the suspended solids just upstream of the discharge point and the suspended solids introduced in the effluent stream:

$$TSS_{mix} = \frac{TSS_u Q_u + TSS_e Q_e}{Q_u + Q_e} \quad (4-66)$$

where:

TSS_{mix}	=	adjusted total suspended solids concentration, mg/L
TSS_u	=	total suspended solids concentration at a point just upstream of effluent discharge, mg/L
TSS_e	=	total suspended solids concentration in effluent discharge, mg/L
Q_u, Q_e	=	upstream harmonic mean flow and effluent discharge flow rates, L/hr

The suspended solids partition coefficient in the mixing zone is a function of the organic carbon partition coefficient of the contaminant and the organic carbon fraction of suspended solids:

$$Kd_{mix} = Koc OC_{mix} \quad (4-67)$$

where:

- Kd_{mix} = suspended sediment-water partition coefficient in the mixing zone, L/kg
- Koc = compound specific organic carbon partition coefficient, L/kg
- OC_{mix} = organic carbon content of suspended sediments in the mixing zone, unitless

This organic carbon content can be solved as the weighted average concentrations of the organic carbon contents of the suspended solids in the effluent discharge and the suspended solids of the receiving water body:

$$OC_{mix} = \frac{TSS_u Q_u OC_u + TSS_e Q_e OC_e}{TSS_u Q_u + TSS_e Q_e} \quad (4-68)$$

where:

- OC_{mix} = organic carbon content of suspended solids in mixing zone, unitless
- TSS_u = total suspended solids concentration at a point just upstream of effluent discharge, mg/L
- TSS_e = total suspended solids concentration in effluent discharge, mg/L
- Q_u, Q_e = upstream harmonic mean flow and effluent discharge flow rates, L/hr
- OC_u, OC_e = organic carbon contents of suspended solids upstream of the discharge point and within effluent discharge stream

Fish lipid concentrations for this solution are then given as:

$$C_{lipid} = BSSAF \frac{C_{ssed}}{OC_{mix}} \quad (4-69)$$

where:

C_{lipid}	=	fish lipid concentration, mg/kg
BSSAF	=	biota suspended solids accumulation factor, unitless
C_{ssed}	=	concentration of dioxin-like compounds on suspended sediments, mg/kg
OC_{mix}	=	organic carbon content of suspended sediments, unitless

Finally, whole fish concentrations are simply this lipid concentrations times a fraction of fish lipid, or $C_{lipid} * f_{lipid}$.

The harmonic mean flow, Q_e , is distinct from the long term average flow. To understand the difference, the following discussion is offered. Assume, for this discussion, that the effluent flow, Q_e , is much lower than the receiving water body flow, Q_i , and therefore it can be neglected. The daily average total water concentration to which a fish is exposed, C_i , is then a function of the daily mass of chemical released, $MASS_i$, divided by the average flow for that day, Q_i :

$$C_i = \frac{MASS_i}{Q_i} \quad (4-70)$$

Bioconcentration factors are multiplied by an average concentration, C_{avg} , over n days. Assuming the loading is constant, $MASS_i = MASS$, then the average concentration is given as:

$$C_{avg} = \frac{1}{n} \sum \frac{MASS}{Q_i} \quad (4-71)$$

This is equivalent to:

$$C_{avg} = \frac{MASS}{Q_H} \quad (4-72)$$

where Q_H is the harmonic mean flow defined by:

$$\frac{1}{Q_H} = \frac{1}{n} \sum \frac{1}{Q_i} \quad (4-73)$$

This is different from the arithmetic average flow, Q_{avg} (i.e., mean flow):

$$Q_{avg} = \frac{1}{n} \sum Q_i \quad (4-74)$$

To see how these numbers would differ, consider 10 daily average flows of 1, 1, 1, 1, 2, 2, 3, 4, 7, 10. The Q_H is calculated as 1.72, whereas the Q_{avg} is calculated as 3.20. The difference is further illustrated by considering the effect on the calculation of the concentration to which one would apply the bioconcentration factor. If the daily load were 10.0, then the sequence of water concentrations would be 10, 10, 10, 10, 5, 5, 3.3, 2, 1.4, and 1. The average concentration is 5.77, and this is the appropriate concentration to use with a bioconcentration factor. If the daily load of ten were divided by the Q_H of 1.72, one would arrive at this correct concentration, but if the daily load were divided by the average flow of 3.2, the incorrectly calculated average concentration would be 3.1.

The key model parameter for the effluent discharge model is the BSSAF. A value of 0.09 for 2,3,7,8-TCDD was assumed for BSAF based on data from Lake Ontario. One important difference between the Lake Ontario ecosystem and the effluent discharge source category is that the impact to Lake Ontario is thought to be principally historical (EPA, 1990b), while for the effluent source category, the impact is, by definition, ongoing. This difference may translate to differences in assignment of BSSAF as compared to BSAF. Consider two aquatic settings where bottom sediments are found to have equal concentrations of dioxin-like compounds - one in

which contamination is ongoing and one in which contamination is primarily in the past. For the aquatic setting where contamination occurred in the past, water column and suspended sediment concentrations would be lower as compared to the aquatic setting where contamination is ongoing, because water column impacts are only a function of depuration of bottom sediments for the historically impacted water body. It is certainly arguable that exposure of aquatic organisms is greater in the ecosystem where impacts are ongoing, as compared to a system where impacts are historical, when bottom sediment concentrations are equal in the two systems. Now recall the assumption made for the soil contamination and stack emission source categories (in both cases the water body impact is ongoing) concerning the relationship between suspended and bottom sediments - that the organic carbon normalized concentrations are equal. If this is a valid assumption for a system with ongoing impacts, and if in fact fish are relatively more exposed when impacts are ongoing rather than historical, then this argues that a BSSAF for an ongoing contamination setting should be greater in numerical value than a BSAF for a setting where contamination was historical.

However, no data could be found to support such a hypothesis, and there would be no numerical basis for an assumed difference between BSAF and BSSAF. For this reason, the values assumed for BSSAF and BSAF are equal for this assessment. It should be noted that all bioconcentration or biotransfer parameters, such as the BSSAF, are qualified as second order defaults for purposes of general use. Section 6.2. of Chapter 6 discusses the use of parameter values selected for the demonstration scenarios, including a categorization of parameters. Second order defaults are defined there as parameters which are theoretical and not site specific, but whose values are uncertain in the published literature. The parameter values in this category should be considered carefully by users of the methodology.

The effluent discharge solution algorithm was evaluated using data and information from the 104 pulp and paper mill study (EPA, 1990c), which measured discharges of 2,3,7,8-TCDD from 104 mills in 1988, and from the National Study of Chemical Residues in Fish (NSCRF; EPA, 1992a), which measured fish tissue concentrations of 2,3,7,8-TCDD at points downstream from several of these mills. A third modeling study (EPA, 1990d) collected critical data for this modeling evaluation, such as harmonic mean flows downstream of the mills. Finally, the National Council for Air and Stream Improvement (NCASI) provided details on their assessment of this data, which was used here. Importantly, this information included linking specific fish samples to specific mills. A full description of this modeling evaluation is in Chapter 7, Section 7.2.3.6.

There was a dichotomy of model performance as a function of the size of the receiving water body. For most of the mills, the receiving water bodies had harmonic mean flows around 10^8 L/hr, with a range of 10^7 to 10^9 L/hr. A small number of mills, however, discharged into more substantial receiving water bodies which had an average flow of 5×10^{10} L/hr. Comparing model predictions of fish tissue concentrations for mills discharging into the smaller water bodies, it was found that the model tended to underpredict fish tissue concentrations - the average predicted whole fish concentration was near 7 ppt, whereas the average observed whole fish concentration was near 15 ppt. The same was not true for the large receiving water bodies. In that case, the average whole fish tissue concentration observed was an order of magnitude or more higher than predicted whole fish concentration. No precise explanation could be given for this result. The most likely explanation is that, for these large water bodies, there were other sources of dioxin releases. This comparative exercise did assume inherently that the effluent discharge was the sole source of fish tissue concentrations of 2,3,7,8-TCDD.

It was noted that, for the smaller receiving water bodies, an increase in the assumed BSSAF of 0.09 (which was the value of BSAF assumed otherwise in this assessment) to 0.20 resulted in an average model prediction of fish tissue concentration of near 15 ppt, essentially the same as the observed fish concentration. This could be some empirical evidence for the argument developed above - that the BSSAF for a system with ongoing impacts should be greater in numerical value than a BSAF developed from data on an ecosystem where impacts were primarily historical.

In any case, parameters for the demonstration scenario in Chapter 5 for this source category were derived from 104-mill data. Data from only 77 of the mills was used for the following parameter developments. Mills not included are: 1) the ten mills discharging into the largest water bodies, 2) 9 mills for which EPA (1990d) was unable to derive harmonic mean flows from STORET data, and 3) 8 mills for which data on total suspended solids content in the effluent stream was unavailable from EPA (1990c; actually 11 mills did not suspended solids data, but three were in other categories deleted).

Values of model parameters for the demonstration are now summarized:

- **TSS_u, TSS_e:** The average upstream total suspended solids term from the 77 mills, TSS_u, was 9.5 mg/L. The average suspended solids concentration within the effluent streams from the 77 mills was 70 mg/L.

- **OC_u, OC_e:** No information was available on the organic carbon content of the suspended solids upstream of the effluent discharge point. A value of 0.05 was assigned, which was the value assigned for other source categories. No data as well could be found for the

organic carbon content of the effluent solids. However, such solids are essentially biosolids from biological treatments of mill sludges. The organic carbon content of such solids is expected to be much higher than 0.05. The value recommended for OC_e was 0.36 (Steven Hinton, PhD., P.E., National Council of the Paper Industry for Air and Stream Improvement, Inc.; Department of Civil Engineering, Tufts University, Medford, MA 02155). This was based on an average proportion of carbon in algal biomass of 0.36 given in Morel (1983).

- **Q_u, Q_e :** Flow values for the receiving water and effluent stream were summarized in EPA (1990d). The average effluent flow rate, Q_e , for the 77 mills was $4.10 * 10^6$ L/hr, and the average harmonic mean flow for the receiving water body, Q_u , was $4.65 * 10^8$ L/hr.

- **$K_{oc}, BSSAF, f_{lipid}$:** Values of K_{oc} and f_{lipid} are the same ones which have been used for the other source categories. As discussed in the introduction to this section, the Biota Suspended Solids Accumulation Factor, BSSAF, will be assumed to be the same as the Biota Sediment Accumulation, BSAF. This value is 0.09 for 2,3,7,8-TCDD.

- **$MASS_c$:** The mass of 2,3,7,8-TCDD exiting from the 77 mills averaged 0.197 mg/hr. However, this data was pertinent for 1988. Since then, pulp and paper mills have reduced the discharge of dioxin-like compounds in their effluents by altering the pulp bleaching processes. Gillespie (1992) reports that data on effluent quality from all 104 mills demonstrate reductions in discharges of 2,3,7,8-TCDD of 84%. On this basis, the value of $MASS_c$ for all three example compounds will be 0.0315 mg/hr (16% of 0.197 mg/hr).

Using these parameters in the simple dilution model for 2,3,7,8-TCDD results in the following:

- 1) If the mass loadings of 2,3,7,8-TCDD are assumed to be fully sorbed to solids in the effluent discharge, and not to exist in the soluble phase in the discharge, than the concentration of 2,3,7,8-TCDD on discharging effluent solids is $1.1 * 10^{-4}$ mg/kg, or 110 ppt.

- 2) The total suspended solids concentration in the mixing zone, TSS_{mix} , equals 10.0 mg/L. The organic carbon content of suspended solids in the mixing zone, OC_{mix} , is estimated as 0.069. It is seen how the effluent discharge influences these two key quantities: the unadjusted TSS_u was given as 9.5 mg/L, and the unadjusted OC_u was 0.05.

- 3) The overall suspended solids concentration of 2,3,7,8-TCDD in the mixing zone after mixing and equilibrating with surrounding water, C_{ssed} , was 4.5 ppt. This compares to the concentration that might be on the effluent solids of 110 ppt, indicating more than an order of magnitude reduction in concentration by mixing with solids of the receiving water body, and partitioning into the water column.

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Table 4-1. Available Biota to Sediment Accumulation Factors, BSAF, for dioxin-like compounds.

Reference/Congener	Fish Species	Water Body	# Sed. Samples # Fish Samples	BSAF	Comments
Kuehl, et al., 1987 2378-TCDD 2378-TCDF 12378-PCDD 1234/678-HxCDD 123678-HxCDF 1234678-HpCDD 1234678-HpCDF	Carp	Wisconsin River	1/1	0.27 0.06 0.06 0.035 0.037 0.0048 0.0033	Laboratory flow through experiment using Wisconsin River sediment and Lake Superior water; BSAFs determined from one "representative" sediment sample and one "composited" fish sample; sediment organic carbon and fish lipid contents given in article; no other details provided.
US EPA, 1990b 2378-TCDD 2378-TCDD 2378-TCDD 2378-TCDD 2378-TCDD	Brown Trout Lake Trout Smallmouth Bass White Perch Yellow Perch	Lake Ontario	55/81 55/81 55/14 55/38 55/77	0.03 0.07 0.05 0.20 0.03	Comprehensive field study on bioaccumulation of 2378-TCDD in Lake Ontario; BSAFs are estimated given 55 sediment samples and specific number of fish samples as noted; report evaluates matching fish with sediment data from sites where fish were caught
Parkerton, 1991 2378-TCDD 2378-TCDD 2378-TCDD	Resident Fish Migratory fish Blue Crab	Passaic River	61/11 61/15 61/14	0.081 0.009 0.055	7 "resident" fish species were best represented by carp; "migratory" species were eel and striped bass; TCDD contamination attributed to historical industrial input, particularly a 2,4,5-T plant operation from 1940s to 60s.

Table 4-1. (Cont'd)

Reference/Congener	Fish Species	Water Body	# Sed. Samples # Fish Samples	BSAF	Comments
Kjeller, et al, 1990	Pike	Lake Vanern			Results presented at right derived from data in Kjeller, et al (1990); data includes sediment samples from four sites in Lake Vanern and 6 composited (2-5 fish in composite) pike associated with the four sites; pike concentrations reported in article on a lipid basis; Lake Vanern is near a paper mill.
2378-TCDD			4/6	2.94	
12378-PCDD			4/6	1.03	
123478-HxCDD			4/6	0.17	
123678-HxCDD			4/6	0.086	
123789-HxCDD			4/6	0.018	
OCDD			4/6	0.002	
2378-TCDF			4/6	1.40	
1234/78-PCDF			4/6	0.25	
23478-HxCDF			4/6	0.71	
123478/9-HxCDF			4/6	0.036	
123678-HxCDF			4/6	0.065	
123789-HxCDF			4/6	0.27	
234678-HxCDF			4/6	0.047	
1234678-HpCDF			4/6	0.0009	
1234789-HpCDF			4/6	0.023	
1234678-HpCDF			4/6	0.006	
OCDF			4/6	0.0001	

Table 4-1. (Cont'd)

Reference/Congener	Fish Species	Water Body	# Sed. Samples # Fish Samples	BSAF	Comments
US EPA, 1993b 2378-TCDD 2378-TCDD 2378-TCDD 2378-TCDD 2378-TCDD 2378-TCDD 2378-TCDD	 Smelt Sculpin Herring Gull Bullhead Sandworm Clam Shrimp	 different bodies	 NA	 0.04 0.12 0.43 0.05 0.48 0.93 0.73	 Results compiled in EPA (1993) for 2378-TCDD; details found in these studies: Batterman, et al. (1989) Batterman, et al. (1989) EPA (1990b) and Braune, Norstrom (1989) Cook (unpublished) as listed in EPA (1993b) Rubinstein, et al. (1983) Rubinstein, et al. (1983) Rubinstein, et al. (1983)
CDEP, 1992 2378-TCDD 2378-TCDF 23478-PCDF I- TEQ	 See "Comment"	 23 different bodies	 346/521 346/521 346/521 346/521	 0.86 0.25 0.47 0.24	 Data supplied by Connecticut DEP; complete data description in Chapter 7 of this assessment; study designed to evaluate newly operating resource recover facilities. BSAFs are calculated based on 521 fish samples including the species: carp, channel catfish, white catfish, white sucker, brown bullhead, yellow perch

Table 4-1. (Cont'd)

Reference/Congener	Fish Species	Water Body	# Sed. Samples # Fish Samples	BSAF	BEF	Comments
US EPA, 1995	Lake Trout	Lake Ontario	NA			EPA (1995) claims that the Lake Ontario data from EPA (1990b) was reanalyzed for the suite of dioxin-like congeners. It is not clear why the 2378-TCDD for lake trout was 0.059 in this study but listed as 0.07 for lake trout in EPA (1990b). It is also not clear how many samples of fish and sediment were reanalyzed for the data on the right. Also listed to the left are the "bioequivalency factors", or BEFs, as listed in EPA (1995) and as developed from this data set. See text for more detail.
2378-TCDD				0.059	1.00	
12378-PCDD				0.054	0.92	
123478-HxCDD				0.018	0.31	
123678-HxCDD				0.0073	0.12	
123489-HxCDD				0.0081	0.14	
1234678-HpCDD				0.0031	0.051	
OCDD				.00074	0.012	
2378-TCDF				0.047	0.80	
12378-PCDF				0.013	0.22	
23478-PCDF				0.095	1.6	
123478-HxCDF				0.0045	0.076	
123678-HxCDF				0.011	0.19	
123789-HxCDF				0.037	0.67	
234678-HxCDF				0.04	0.63	
1234678-HpCDF				.00065	0.011	
1234789-HpCDF				0.023	0.39	
OCDF				.00099	0.016	

Table 4-2. Available Biota to Sediment Accumulation Factors, BSAF, for PCBs.

Reference/Congener	Fish Species	Water Body	BSAF	Comments
EPA (1990b) PCB	trout, salmon, perch, bass	Lake Ontario	1.40, 0.77, 0.52, 0.86, 3.35, 1.42	These BSAF were compiled in EPA (1990b) from several data sources, years of study, and fish species. The summary provided was not specific in terms of BSAFs associated with specific fish species. It is assumed that "PCBs" described in EPA (1990b) meant "total PCBs". There was one BSAF of 0.58 derived in EPA (1990b) for Aroclor 1254
EPA (1995) Total PCBs PCB 105 PCB 118 PCB 156 PCB 180	Trout	Lake Ontario	1.85 2.70 4.09 3.97 3.78	EPA (1995) used the data of Oliver and Niimi (1988) to derive the BSAFs listed for total PCBs and the PCB congeners. EPA (1995) also lists BSAFs for numerous other non-dioxin-like PCB congeners.
EPA (1995) PCB 77 PCB 105 PCB 118 PCB 126 PCB 167 PCB 180 PCB 189	Trout	Lake Ontario	0.29 4.49 1.72 3.21 0.69 3.26 0.71	EPA (1995) derived these BSAFs based on their reanalysis of sediment and trout data from the original Lake Ontario study (1990b). EPA (1995) also lists BSAFs for numerous other non-dioxin-like PCB congeners.

Table 4-2. (cont'd)

Reference/Congener	Fish Species	Water Body	BSAF	Comments
EPA (1995) PCB 77 PCB 105 PCB 118 PCB 167 PCB 180 PCB 189	Brown Trout	Green Bay, WI	4.12 5.35 4.96 16.0 10.96 3.45	EPA (1995) derived these BSAFs from data on lake trout from the Green Bay. The study from which these data came from was described as EPA's Green Bay/Fox River Mass Balance Study which involved extensive sampling of water, sediment and fish in 1989. No further citation was provided in EPA (1995) for this study.
Parkerton, et al (1993) trichloro-PCB tetrachloro-PCB pentachloro-PCB hexachloro-PCB heptachloro-PCB octachloro-PCB	lake trout, whitefish	Siskiwit Lake	0.45-2.6 0.71-1.3 3.4-9.4 2.9-20.8 12.5 2.2-12.7	Compiled by Parkerton, et al. (1993) from data in Swackhammer, et al. (1988) and Swackhammer and Hites (1988); Parkerton presents data for individual congeners - summary at left aggregates by chlorination and includes both fish species; only one data point presented by heptachloro-PCB.
Parkerton, et al (1993) Total PCBs	Three species of marine fish	Rio de La Plata, Argentina	4.40	Determined by Parkerton, et al (1993) from Columbo, et al (1990) on total PCBs. Columbo reference has data on PCBs 5-8, 14, 19, 28-31, 52, 101, 110, 138, 153, 180.

Table 4-2. (cont'd)

Reference/Congener	Fish Species	Water Body	BSAF	Comments
Parkerton, et al (1993)	flounder, lobster, crab	New Bedford Harbor		Compiled by Parkerton, et al. (1993) from data in BOS (1990); summary at left is the range of values for PCB congener groups, and averaged across the noted species.
dichloro-PCB			0.11-0.59	
trichloro-PCB			0.26-0.65	
tetrachloro-PCB			0.65-1.02	
pentachloro-PCB			1.05-2.08	
hexachloro-PCB			1.29-4.00	
heptachloro-PCB			0.84-2.74	
octachloro-PCB			0.23-1.17	
nonachloro-PCB			0.02-0.38	

Table 4-3. Data and parameters used to determine the part of the plant concentration which was due to the deposition of particle bound dioxins (see below table for definition of columns).

#1	#2	#3	#4	#5	#6	#7	#8
Cl ₄ DD	0.51/0.49 (0.90/0.10)	0.029	0.0141	0.007	0.13	0.123	94
Cl ₅ DD	0.13/0.87 (0.72/0.28)	0.029	0.0251	0.013	0.13	0.117	90
Cl ₆ DD	0.03/0.97 (0.55/0.45)	0.053	0.0513	0.027	0.14	0.113	81
Cl ₇ DD	0.01/0.99 (0.23/0.77)	0.088	0.0873	0.046	0.13	0.085	65
OCDD	0.002/0.998 (0.07/0.93)	0.163	0.1629	0.084	0.19	0.106	56
Cl ₄ DF	0.53/0.47 (0.91/0.09)	0.190	0.0887	0.046	0.63	0.584	93
Cl ₅ DF	0.20/0.80 (0.78/0.22)	0.104	0.0827	0.043	0.25	0.208	83
Cl ₆ DF	0.06/0.94 (0.52/0.48)	0.082	0.0766	0.040	0.15	0.110	74
Cl ₇ DF	0.02/0.98 (0.23/0.77)	0.057	0.0559	0.029	0.14	0.111	79
OCDF	0.002/0.998 (0.11/0.89)	0.026	0.0259	0.014	0.029	0.016	54

Column Definition:

- #1 - Congener Group
- #2 - Vapor/Particle Fractions. Ratios in parenthesis were the fractions measured in the 2-stage air sampling equipment. See text for more detail.
- #3 - Total air concentration, pg/m³
- #4 - Particle bound air concentration, pg/m³
- #5 - Plant concentration calculated to be due to particle deposition, ng/kg fresh
- #6 - Total plant concentration, ng/kg fresh
- #7 - Plant concentration calculated to be due to vapor transfer, estimated as Column 6 - Column 5, ng/kg fresh
- #8 - Percent of plant concentration due to vapor transfers.

Table 4-4. Development of the B_{vpa} using data of Welsch-Pausch, et al (1995) compared against the B_{vpa} as developed in EPA (1994) (see below table for column definitions).

# 1	# 2	# 3	# 4	# 5	# 6
Cl ₄ DD	94400	0.0149	6.35*10 ⁶	6.55*10 ⁴	1.0*10 ⁵
Cl ₅ DD	90100	0.0039	2.32*10 ⁷	2.39*10 ⁵	6.3*10 ⁵
Cl ₆ DD	87300	0.0017	5.05*10 ⁷	5.20*10 ⁵	6.9*10 ⁵ - 2.3*10 ⁶
Cl ₇ DD	65200	0.00074	8.83*10 ⁸	9.10*10 ⁶	1.0*10 ⁷
OCDD	81300	0.00036	2.25*10 ⁸	2.36*10 ⁶	2.4*10 ⁹
Cl ₄ DF	450000	0.101	4.44*10 ⁶	4.57*10 ⁴	1.5*10 ⁵
Cl ₅ DF	159000	0.0168	9.47*10 ⁶	9.75*10 ⁴	3.8*10 ⁵ - 5.3*10 ⁵
Cl ₆ DF	84900	0.0054	1.57*10 ⁷	1.62*10 ⁵	5.9*10 ⁵ - 1.4*10 ⁶
Cl ₇ DF	85400	0.00106	8.05*10 ⁸	8.30*10 ⁶	6.8*10 ⁵
OCDF	12000	0.000054	2.21*10 ⁸	2.28*10 ⁶	1.7*10 ⁸

Column Definitions:

- #1 - Congener
- #2 - Vapor phase volumetric grass concentration, pg/m³
- #3 - Vapor phase volumetric air concentration, pg/m³
- #4 - B_{vol} calculated from the data of Welsh-Pausch, et al (1995)
- #5 - B_{vpa} calculated from the data of Welsh-Pausch, et al (1995)
- #6 - B_{vpa} as developed in EPA (1994). These B_{vpa} were calculated for the individual dioxin-like congeners. Where a range is presented, such as for Cl₆DF, this was the range for the dioxin-like congeners in the congener group.

Table 4-5. Ratios of dioxins and furans in milk fat (MF) and body fat (BF) to concentrations in diets of farm animals.

Animal	Days	Compound	BF:Diet	MF:Diet	Reference
Goats	56	2378-TCDD	-	2.8	Arstilla et al. (1981)
Cows	21	2378-TCDD	-	4.4	Jensen & Hummel (1982)
Cows	70	123678-HxCDD	3.9	5.7	Firestone, et al (1979)
		1234678-HpCDD	0.4	0.6	
		OCDD	0.1	0.1	
Steers	28	2378-TCDD	3.5	-	Jensen, et al (1981)
Heifers	160	123678-HxCDD	2.1	-	Parker, et al (1980)
		1234678-HpCDD	0.2	-	
		OCDD	0.05	-	
		1234678-HpCDD	0.3	-	
		OCDF	0.1	-	
Cow	92	2378-TCDD	-	5.76	McLachlan, et al. (1990) ¹
		12378-PCDD	-	5.55	
		123478-HxCDD	-	2.69	
		123678-HxCDD	-	2.32	
		123789-HxCDD	-	2.99	
		1234679-HpCDD	-	0.27	
		1234678-HpCDD	-	0.48	
		OCDD	-	0.69	
		234/78-TCDF	-	1.25	
		1234/78-PCDF	-	0.97	
		23478-PCDF	-	4.13	
		123478/9-HxCDF	-	3.12	
		123678-HxCDF	-	2.67	
		234678-HxCDF	-	2.37	
		1234678-HpCDF	-	0.55	
		1234789-HpCDF	-	1.32	
		OCDF	-	0.27	
		I-TEQ	-	3.33	

Table 4-5. (Cont'd)

Animal	Days	Compound	BF:Diet	MF:Diet	Reference
Cows		2378-TCDD		7.1	Fries, et al. (1999) ²
		12378-PCDD		5.0	
4 cows	28,	123478-HxCDD		3.1 (3.6)	
and three	42,	123678-HxCDD		3.7 (3.2)	
times	56	123789-HxCDD		2.6 (2.2)	
during		1234678-HpCDD		0.68 (0.3)	
milking		OCDD		0.08 (0.05)	
for each		23478-PCDF		3.5 (3.5)	
cow		123478-HxCDF		3.0 (1.1)	
		123678-HxCDF		3.1 (2.2)	
		234678-HxCDF		1.9 (1.6)	
		1234678-HpCDF		0.72 (0.3)	
		1234789-HpCDF		0.87	
		OCDF		0.07 (0.01)	

¹ McLachlan, et al. (1990) was not a dosed feeding study; the single cow studied was given normal rationing. The first sample was taken Feb 16, 1989, two months after the last calving on Dec. 22, to maximize the possibility that steady state had been reached. The 92 days listed was from Dec. 22 until the last sample on Mar. 24.

²Fries, et al. (1999) were derived from a study where ground up PCP-treated wood was added to the cows' feed. Results are presented only for congeners where concentrations were above background for both milk and feed. Comparison with BCFs derived for other cows which were fed a normal diet (without PCP-treated wood) setting were comparable to the feeding experiment; these background BCFs are shown in parenthesis

Source: Fries and Paustenbach (1990), McLachlan, et al. (1990), and Fries, et al. (1999)

Table 4-6. Ratios of PCBs in milk fat (MF) and body fat (BF) to concentrations in diets of lactating cows^a.

Animal	Days	Compound	Concentration in diet, ppm	BF:diet	MF:diet	Reference and Comments
Lactating Cows	20 40 60	Aroclor 1254 Aroclor 1254 Aroclor 1254	12.1 12.1 12.1	- - 3.4	3.1 4.4 4.8	Fries, et al (1973)
Lactating Cows	56	dichloro-PCBs tetrachloro-PCBs pentachloro-PCBs hexachloro-PCBs heptachloro-PCBs octachloro-PCBs nanochloro-PCBs	0.05 0.001 0.003 0.009 0.010 0.005 0.001	- - - - - - -	0.4 5.9 1.2 2.2 2.3 3.8 4.0	Tuinstra et al (1981), data is: average of 2 congeners one congener average of 2 congeners average of 7 congeners average of 8 congeners average of 5 congeners one congener
Lactating Cows	60 120 180	Aroclor 1254 Aroclor 1254 Aroclor 1254	0.51 2.82 18.97	2.8 2.4 3.7	3.7 3.9 4.8	Willett, et al. (1987) values at left reflect different average intake over 3 periods.
Lactating Cows	20	Aroclor 1254	2.56	-	1.2	Willett and Liu (1982)
Lactating Cows	32	Aroclor 1254	10.25	-	4.2	Perry, et al (1981)

^a see text for full details of noted studies.

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Table 4-7. BCFs for liver, adipose, thigh meat, and eggs calculated from the Cal-EPA experiments.

Congener	Low Exposure Group				High Exposure Group			
	Liver	Adipose	Thigh	Egg	Liver	Adipose	Thigh	Egg
2378-TCDD	NA	NA	NA	NA	63.4	28.8	28.7	11.3
12378-PCDD	13.7	11.7	6.8	6.0	44.3	23.7	21.5	8.9
123478-HxCDD	6.7	7.6	3.6	5.4	37.3	18.3	15.9	8.5
123678-HxCDD	10.7	11.0	5.6	10.2	26.8	12.5	9.9	7.0
123789-HxCDD	6.1	5.1	2.4	4.5	16.0	7.4	5.4	4.4
1234678-HpCDD	7.6	2.7	1.4	4.8	22.3	4.1	3.3	4.8
OCDD	3.1	0.6	0.3	4.3	14.9	0.7	0.4	1.8
2378-TCDF	8.1	2.7	3.1	2.7	42.6	18.0	21.9	6.8
12378-PCDF	36.2	27.7	18.0	20.5	NA	NA	NA	NA
23478-PCDF	16.2	13.1	7.4	7.8	59.8	26.7	28.4	10.6
123478-HxCDF	13.8	11.9	4.8	7.4	46.8	15.1	13.4	8.5
123678-HxCDF	10.9	11.7	5.3	8.2	37.8	16.9	14.2	8.5
123789-HxCDF	NA	NA	NA	NA	NA	NA	NA	NA
234678-HxCDF	8.2	4.8	2.1	3.0	33.4	8.3	6.8	5.1
1234678-HpCDF	4.2	2.4	1.0	3.1	15.3	3.3	2.7	3.9
1234789-HpCDF	3.8	1.8	0.9	2.2	26.5	5.2	4.2	4.6
OCDD	1.9	0.5	0.3	1.4	11.4	0.8	0.1	1.5

NA = described as “not applicable” for derivation of BCFs by Stephens, et al. (1995) because one or both measurements were below the quantification limit.

Table 4-8. Chicken and egg BCFs for Aroclor mixtures.

Aroclor Mixture	Low Exposure Group		High Exposure Group	
	Egg	Body Fat	Egg	Body Fat
1221	NA	NA	0.4	1.2
1232	NA	NA	1.2	2.6
1242	3.5	2.9	7.2	4.5
1248	3.5	9.8	4.7	4.5
1254	6.5	7.4	5.7	6.2
1268	NA	NA	10.8	2.6

NA = data was not taken for the low, 2 ppm, concentration exposure for these Aroclors

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Table 4-9. Ranges of concentrations of PCDDs, PCDFs, and PCBs in municipal waste combustor ash (results in ng/g or ppb; ND = Not detected; NR = not reported; Tr = trace; DL between 0.01 and 0.1 ng/g).

Constituent	Fly ash	Combined ash	Bottom ash	Constituent	Fly ash	Combined ash	Bottom ash
I. DIOXINS				III. PCBs			
MCDD	2.0	ND	NR	Mono CB	0.29-9.5	ND	ND-1.3
DCDD	0.4 - 200	ND-120	NR	Di CB	0.13-9.9	0.13-1.35	ND-5.5
T ₃ CDD	1.1 - 82	ND-33	NR	Tri CB	ND-110	0.35-14.3	ND-80
T ₄ CDD	ND - 250	0.14-14	<0.04-410	Tetra CB	0.5-140	16.5	ND-47
PCDD	ND - 722	0.07-50	ND-800	Penta CB	0.8-225	ND	ND-48
H ₆ CDD	ND - 5,565	0.07-78	ND-1000	Hexa CB	0.45-65	ND-39	NR
H ₇ CDD	ND - 3,030	0.07-120	ND-290	Hepta CB	ND-0.1	ND	NR
OCDD	ND - 3,152	0.07-89	ND-55	Octa CB	ND-1.2	ND	NR
2378-TCDD	ND - 330	0.02-0.78	<0.04-6.7	Nona CB	ND	ND	NR
Total PCDD	5 - 10,883	6.2-350	ND-2800	Deca Cb	ND	ND	NR
II. FURANS				Total PCB	ND-360	ND-32.15	ND-180
MCDF	41	1.1	NR				
DCDF	ND - 90	ND-42	NR				
T ₃ CDF	0.7 - 550	ND-14	NR				
T ₄ CDF	ND - 410	2.3-9	10.1-350				
PCDF	ND - 1800	1.6-37	0.07-430				
H ₆ CDF	Tr - 2,353	1.2-35	ND-920				
H ₇ CDF	Tr - 887	0.62-36	ND-210				
OCDF	ND - 398	0.18-8.4	ND-11				
2378-TCDF	0.05-5.4	0.41-12	ND-13				
Total PCDF	3.73 - 2,396	6.14-153.9	ND-1600				

Source: EPA (1991)

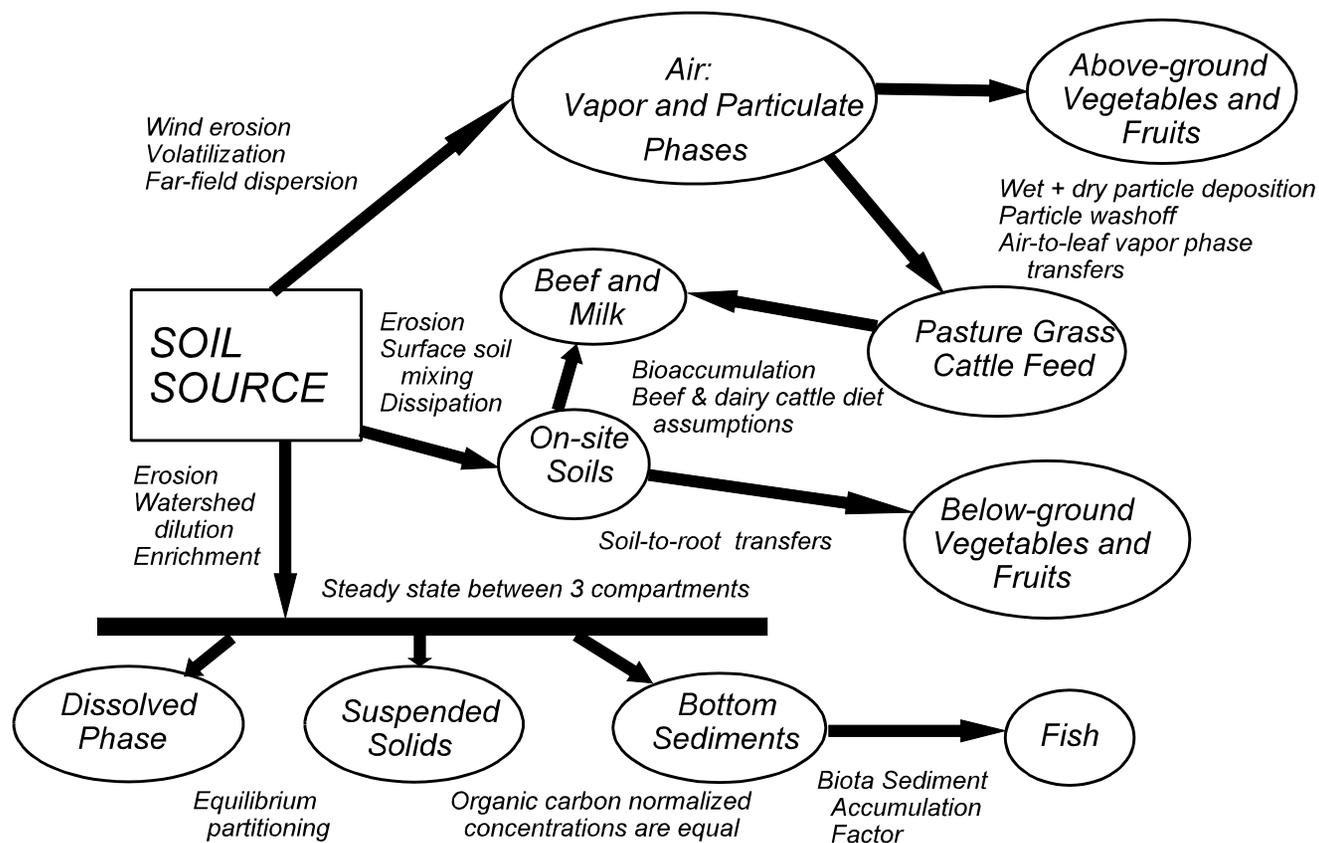


Figure 4-1. Diagram of the fate, transport, and transfer relationships for the soil contamination source category.

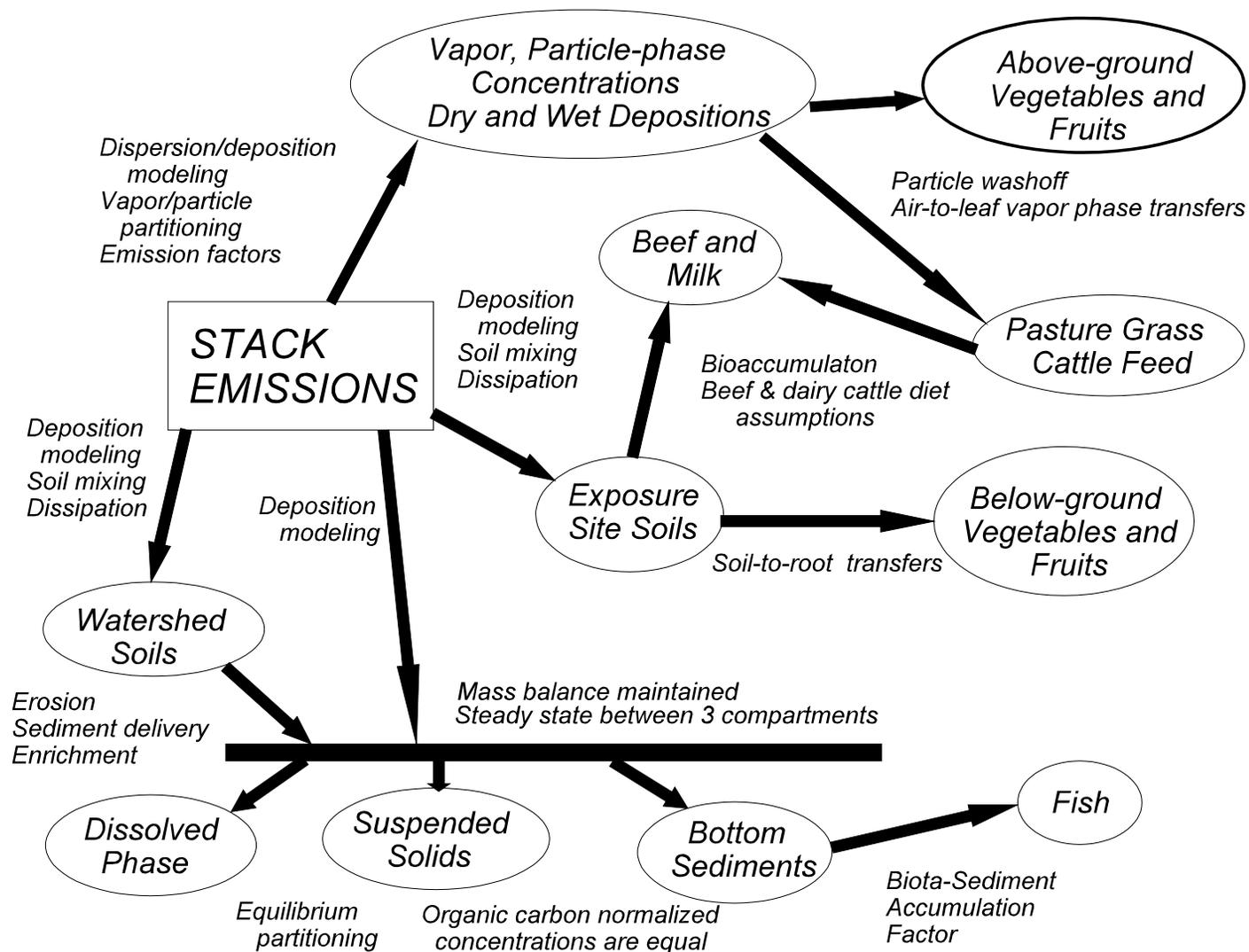


Figure 4-2. Diagram of the fate, transport, and transfer relationships for the stack emission source category.

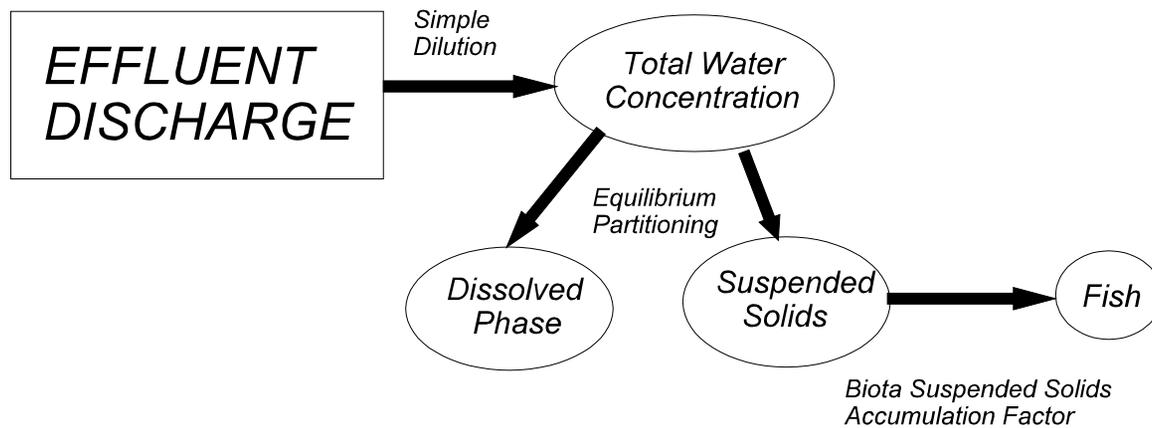
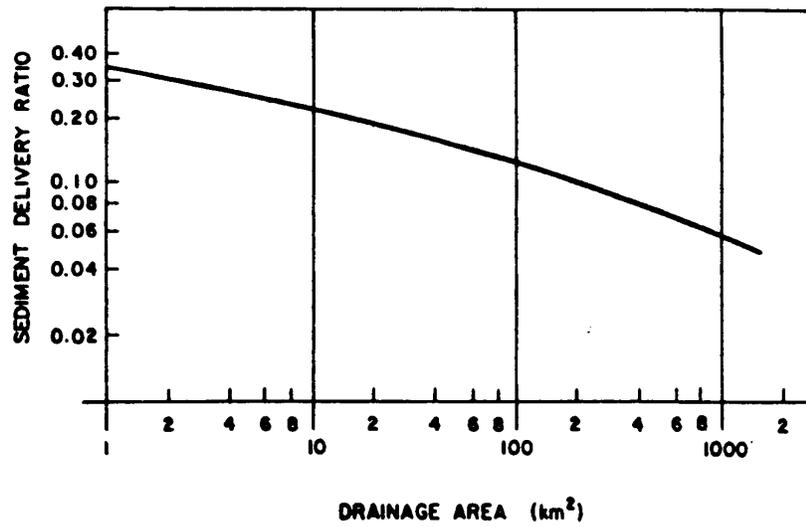


Figure 4-3. Diagram of the fate, transport, and transfer relationships for the effluent discharge source category.



Source: Vanoni, 1975

Figure 4-4. Watershed delivery ratio, SD_w , as a function of watershed size.